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The Influence of Aluminum Salts on the Adsorption of Cationic Polyelectrolyte by Cellulosic Fibers

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THE INFLUENCE OF ALUMINUM SALTS ON THE ADSORPTION OF CATIONIC POLYELECTROLYTE BY CELLULOSIC FIBERS

A thesis submitted by

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SUMMARY

The study of the interactions of aluminum species in papermaking systems has generally been inhibited by the complicated aqueous solution chemistry of the aluminum ion. Recent work on the hydrolysis and precipitation of aluminum by Hayden and Rubin[1] and on the adsorption of aluminum by Arnson[2] has provided a better understanding of aqueous aluminum chemistry and the interactions of aluminum with cellulosic fibers. Using their work as a basis for understanding the interactions of aluminum, this investigation was undertaken to improve the understanding of the interactions between aluminum and the adsorption of cationic polyelectrolyte by cellulosic fibers. An additional benefit of this investigation was an improved understanding of aluminum adsorption.

The adsorption of aluminum chloride, aluminum sulfate, and cationic polyelectrolyte was studied at aluminum concentrations between 2.5×10^{-4}M and 10.0×10^{-4}M, polymer concentrations between 0.3 ppm and 3.0 ppm (0.01 and 0.10% additions), pH between 4.1 and 5.5, and polymer adsorption times between 15 seconds and 10 minutes. A refined, fines-free, oxidized cotton linters pulp was used as the cellulosic substrate. The carboxyl content of the pulp was similar to that of a bleached kraft pulp. A carbon-14 labeled, low charged, high molecular weight polyacrylamide was synthesized as the cationic polyelectrolyte.

As with Arnson's study, the amount of aluminum adsorbed onto cellulosic fibers was observed to be a function of pH, aluminum concentration, and aluminum salt. The anion from the aluminum salt was found to significantly affect the adsorption of the precipitate species. The divalent sulfate anion, when compared with the chloride anion, was observed to lower the cationic charge on the precipitate-covered fiber and to allow greater adsorption. Unlike the earlier study, aluminum adsorption was found to be a function of aluminum concentration throughout the whole pH and concentration range. In agreement with

Arnson's study, a characteristic sharp increase in aluminum adsorption was observed to occur between pH 4 and 5. However, unlike Arnson's study the break in aluminum adsorption correlated with the pH at which aluminum starts to precipitate (pHp). The pHp's for aluminum chloride in the presence of fibers were found to be approximately 1.6 pH units lower than the values cited by Hayden and Rubin and the values determined in this study in the absence of fibers. However, the pHp's for aluminum sulfate were in total agreement.

With the understanding of Hayden and Rubin's aluminum distribution curves, it was possible to consider the adsorption of aluminum and polymer from aluminum salt solutions in two distinct pH regions. The first region was below the pHp where only soluble aluminum species exist. The second region was above the pHp where the aluminum precipitate was predominant.

Below the pHp, for both aluminum salts, the trivalent aluminum ion was concluded to be the dominant adsorbing species. The adsorbed trivalent aluminum ion reduced the polymer adsorption, which was interpreted to be due to a reduction in adsorption rate. The polymer adsorption (i.e., adsorption rate) was a function of aluminum adsorption, and consequently aluminum concentration. Polymer adsorption was found to increase with higher polymer concentrations; however, the relative polymer adsorption decreased. Higher polymer concentrations were also observed to have the same effects in the absence of aluminum, thus indicating that it was not due to the influence of aluminum. The detrimental effects of adsorbed aluminum and on the relative polymer adsorption were apparently due to the occupation of the negative adsorption sites (i.e., carboxyl groups) on the fiber and the raising of the fiber charge. The higher fiber charge would reduce the electrostatic attraction between the fiber carboxyl groups and the cationic polymer.

Above the pHp in the presence of aluminum chloride, the fiber surface became very positively charged due to a layer of adsorbed aluminum precipitate. In this region the relative polymer adsorption was reduced to an extremely low level (≈ 5%). This would be expected from an unfavorable adsorbing surface, such as the highly charged layer of adsorbed aluminum precipitate. The relative polymer adsorption was found to be unaffected by aluminum and polymer concentration. This was interpreted to be due to the extremely high fiber charge, which is unaffected by further aluminum and polymer adsorption. The relative polymer adsorption was, however, affected by polymer adsorption time, thus indicating that the adsorption was not yet in equilibrium.

Above the pHp, in the presence of aluminum sulfate, the fiber surface became positively charged due to an adsorbed layer of aluminum precipitate. However, the fiber charge was not nearly as high as with aluminum chloride. In this region the presence of aluminum sulfate was found to slightly reduce the polymer adsorption, which was interpreted to be due to a reduction in polymer adsorption rate. The polymer was found to be adsorbed directly and indirectly onto the fiber surface. Negative sulfate ions were incorporated into the aluminum precipitate. These sulfate ions were interpreted to serve as adsorption sites and improve the adsorption of polymer onto the adsorbed precipitate layer. It was speculated that the lower fiber charge, as compared with aluminum chloride, and the high indirect adsorption of polymer allowed some of the polymer to eventually become directly adsorbed. However, most of the polymer remained indirectly adsorbed. As with the soluble aluminum species below the pHp, the relative polymer adsorption was observed to decrease with an increase in polymer concentration. This was interpreted to be due to a lower initial fiber charge and higher polymer adsorption, as compared with the aluminum

chloride case, which allowed the adsorbed polymer to significantly increase the fiber charge and reduce the relative polymer adsorption.

In summation, for aqueous conditions similar to those occurring in a papermaking system, the adsorption of aluminum and its influence on polymer adsorption was found to occur in a systematic and predictable manner directly related to and principally governed by the aqueous solution chemistry of the aluminum ion.

INTRODUCTION

Retention of fines, filler, and pigment particles has long been of importance in papermaking for recovery of material costs, improvements of paper properties, and more recently for environmental considerations. This is especially important in the production of fine papers where the fine solids fraction represents 40-50% of the total furnish solids.[3,4] One of the best noncapital methods of improving retention is the use of synthetic polyelectrolytes.

Despite numerous studies on retention and flocculation by cationic polyelectrolytes, the selection and use of polyelectrolytes in a papermaking system is still basically a trial and error process. Past studies have been limited to either model systems or very simplified systems, and, therefore, the research findings are difficult to translate to use in a "real" papermaking system. While such studies are necessary to establish a basic understanding of how polyelectrolytes function, additional studies are needed to establish the effect which other wet-end materials may have on the polyelectrolytes.

One of the most common chemical species found in the wet end that is already known to affect the retention mechanisms of a cationic polyelectrolyte is alum. Retention studies on alum-cationic polyelectrolyte systems[5-13] have shown alum to have differing effects on the retention capabilities of the polyelectrolyte. These effects vary from increased retention, to decreased retention, to little effect at all.

A major factor which has plagued the retention studies on alum-cationic polyelectrolyte systems is the complicated aqueous solution chemistry of the aluminum ion. Under papermaking conditions, aluminum can form a multitude of species. Unfortunately, our knowledge of aqueous aluminum chemistry has

never been sufficient to establish when and to what degree each of the species forms.

Recently, two studies have shed some light on aluminum chemistry. The first study was conducted by Hayden and Rubin[1] and established when and to what degree each of the species formed. The second study, by Arnson,[2] was based on the first study and determined the adsorption properties of each aluminum species on cellulose. Using the work of Hayden, Rubin, and Arnson, and a well-characterized adsorption system, this investigation was undertaken to understand the influence of aluminum salts on the adsorption of a cationic polyelectrolyte by cellulosic fibers. Future studies can then relate polyelectrolyte adsorption to the retention of fine solids.

LITERATURE REVIEW

The review of the literature focuses on three major elements: the aqueous chemistry of aluminum, the adsorption of aluminum by cellulosic fibers and the adsorption of cationic polyelectrolyte. Preceding these three subject areas is a discussion on retention in alum-cationic polyelectrolyte papermaking systems.

RETENTION IN ALUM-CATIONIC POLYELECTROLYTE PAPERMAKING SYSTEMS

There have been several retention studies[5-13] which have included the effect of alum on the retention performance of cationic polyelectrolytes. However, very little can be discerned about the overall effect that alum has on the polymer because of variations in the papermaking systems and ways of studying retention and inadequate information about the conditions and materials used in the studies. Nevertheless, these studies will be reviewed here in order to bring to light the following points: (1) alum has quite varied effects on the retention capabilities of a cationic polyelectrolyte in both fine paper and unbleached paper systems and (2) the effect of alum on the polymer's retention capabilities is not well understood.

Frankle, Sheridan, et al.[5,6] have studied the filler retention of a fine papers furnish (70% bleached softwood kraft, 27% filler clay, and 3% TiO_2) using a dynamic drainage jar. At cationic polymer additions of 1 and 2 lb/t., the addition of alum (10-100 lb/t.) caused a slight increase in retention up to the 20 lb/t. addition level. Further additions of alum had no effect at all.

Moore's studies[7] of a fine papers furnish (95% bleached softwood kraft, 5% TiO_2) have revealed that alum can have quite an erratic effect on retention in an alum-cationic polyelectrolyte papermaking system. He added alum (0-200 lb/t.) to a system containing 2 lb/t. cationic polyacrylamide and found that the retention initially decreased slightly and then rose dramatically to its best retention level at a 200 lb/t. alum addition.

Pelton and Allen[8] have studied the effect of electrolytes on the filler retention of a fine papers furnish (85% 1:1 bleached hardwood kraft: bleached softwood kraft, 15% TiO_2) using a dynamic drainage jar. At a polymer (cationic polyacrylamide) addition of 1 lb/t., the addition of alum (3-800 lb/t.) had no effect up to the 26 lb/t. addition level. However, at higher additions (up to 800 lb/t.), the retention decreased dramatically.

Avery[9] has studied the effect of alum on filler retention of a fine papers furnish (83% 1:1 bleached hardwood kraft:bleached softwood kraft, 17% 1:1 filler clay:TiO_2, 0.4% rosin) using both machine trials and a dynamic drainage jar. He examined two polymers: a cationic polyacrylamide at 0.5 lb/t. and a cationic starch at 10 lb/t. With either polymer an addition of alum (25-200 lb/t.) caused a reduction in filler retention.

Arvela, Swanson, and Stratton[10] studied the effects of polyelectrolyte molecular weight and stock agitation on the filler retention of a fine papers furnish (78% 1:1 bleached hardwood kraft:bleached softwood kraft, 22% 1:1 TiO_2:filler clay) using a highly charged polyacrylamide and the IPC web former. They found that a 20 lb/t. alum addition increased retention at low stock agitation levels and produced no change from the initial retention level at high agitation levels.

Nicke and Hartman[11] studied the influence of alum on the action of synthetic retention agents with a fine papers furnish (bleached aspen sulfate and filler clay) using a dynamic drainage jar. They added alum from 0 to 160 lb/t. When using a cationic polyacrylamide they found that an alum addition up to 40 lb/t. dramatically improved the filler retention. Further additions of alum had little effect. When using polyethylenimine (PEI), a slight improvement in filler retention was observed up to 40 lb/t. alum addition. However, further alum addition with PEI had a slightly detrimental effect.

Studies of unbleached systems have shown alum's effect on cationic polyelectrolytes to be variable. Guender and Auhorn[12] found that adding alum (0-40 lb/t.) to an unbleached system (70% 2:3 softwood kraft: mechanical pulp, 30% china clay) using 0.6 lb/t. of a cationic polyelectrolyte substantially increased the ash content of the sheet. This was true for all three polymers in the study: polyacrylamide, polyamidoamine-epichlorohydrin resin, and modified polyethylenimine. On the other hand, Arnson's[13] studies of fines retention of an unbleached kraft pulp using a dynamic drainage jar showed that the addition of alum (0-160 lb/t.) reduced the retention capabilities of a cationic polyacrylamide (2 lb/t.) by greater than 50% of the value without the alum present.

From the studies of alum-cationic polyelectrolyte papermaking systems one can conclude that the effects of alum on the retention capabilities of cationic polyelectrolytes are quite varied and not well understood.

AQUEOUS ALUMINUM CHEMISTRY

This section presents a brief summary of the aqueous chemistry of dilute aluminum solutions. A detailed review of the literature on this topic

has already been conducted by Arnson.[14] The present state of knowledge on aqueous chemistry of dilute aluminum solutions can best be summarized by reviewing a study by Hayden and Rubin.[1] Their study is probably the most complete on aluminum hydrolysis and precipitation to date and provides the basis for a more precise description of aluminum aqueous equilibria. Their study has examined the chemistry of aluminum both in the absence of complexing anions, by using aluminum nitrate, and in the presence of complexing anions, by using aluminum sulfate. Therefore, the review will consist of two topics: (1) aluminum nitrate and (2) aluminum sulfate.

Aluminum Nitrate

Hayden and Rubin concluded that their experimental data for a non-complexing aluminum salt could only explain the presence of five aluminum species: Al^{3+}, $AlOH^{2+}$, $Al_8(OH)_{20}^{4+}$, $Al(OH)_3$, and $Al(OH)_4^-$. Analysis of potentiometric and turbidity data with a modification of the computer program SCOGS (stability constants of generalized species) allowed them to calculate the mixed stability constants for each of these species. With the equilibrium constants, it is possible to solve for the distribution of the aluminum species as a function of pH (Fig. 1).

The formation of the aluminum species, especially $Al_8(OH)_{20}^{4+}$ and the precipitate, is also a function of aluminum concentration. As the concentration of aluminum increases, $Al_8(OH)_{20}^{4+}$ and the precipitate form at a lower pH and the amount of the polynuclear species at the pHp increases. The effect of aluminum concentration on the pH of precipitate formation (pHp) is shown in Table 1.

In their paper, Hayden and Rubin only present the aluminum species distribution curves at an aluminum concentration, 5.0×10^{-4}M (Fig. 1). In

order to generate the distribution curves at other concentrations, Arnson[14] solved the coupled equilibria by using the Hayden and Rubin equilibrium constants for each aluminum species. The analysis was restricted to pH 4.0-5.5 and aluminum concentrations 1.0×10^{-4} - 10.0×10^{-4}M.

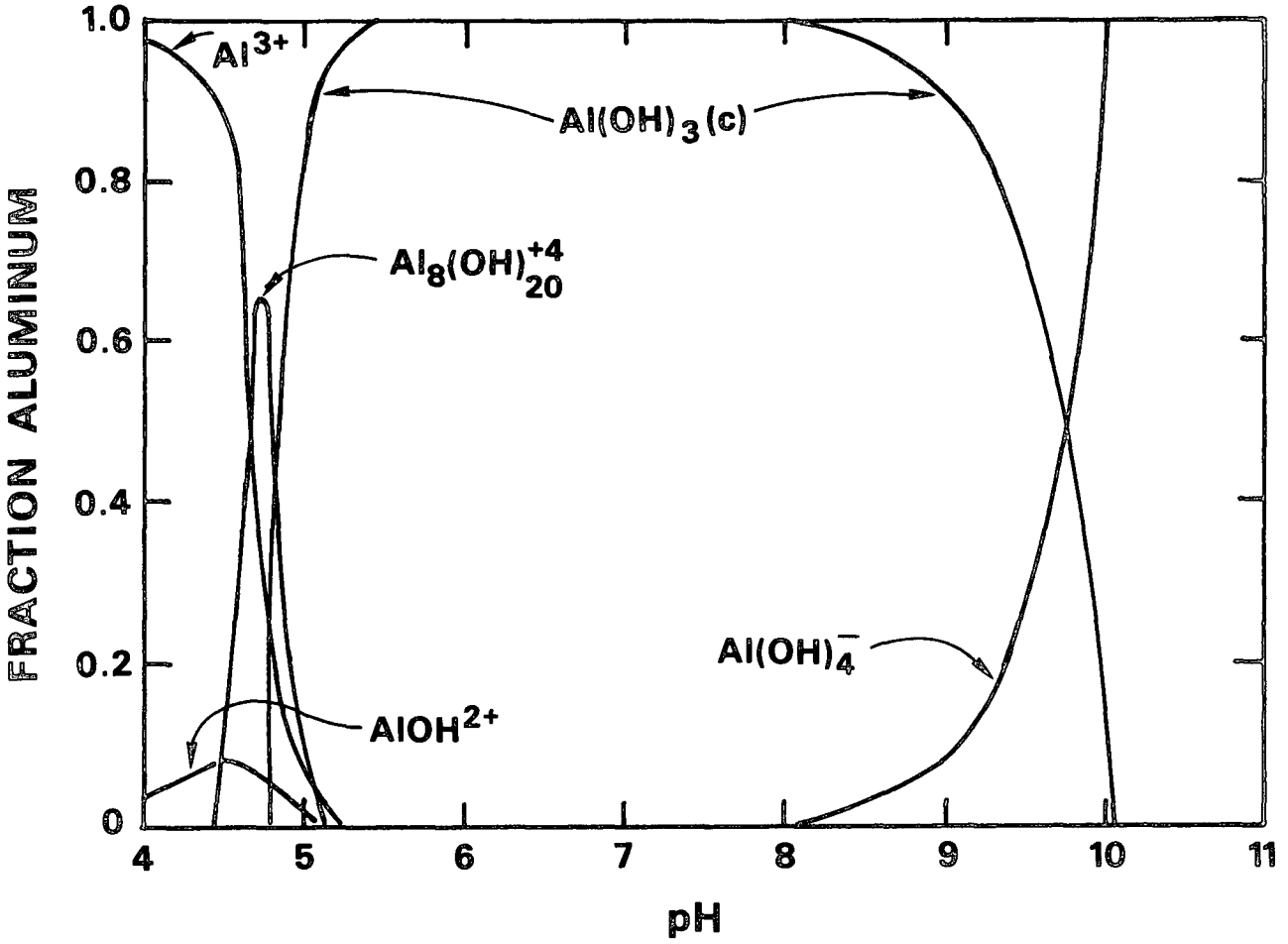

Figure 1. Distribution of aluminum species as a function of pH (5.0×10^{-4}M).[1]

Table 1. Effect of aluminum concentration on the pH of precipitate formation (pHp-exp. observed pH of precipitation at one hour by Hayden and Rubin).

Aluminum Concentration, M	pHp
1.0×10^{-4}	4.88
2.5×10^{-4}	4.76
5.0×10^{-4}	4.66
1.0×10^{-3}	4.57

The distribution curves shown in Fig. 2 are typical results obtained by Arnson from the solution of the equilibria. By restricting the pH range to 4.0-5.5, the number of aluminum species has been reduced to four. The previously mentioned effects of aluminum concentration on the formation of the polynuclear species and the precipitate are also seen in Fig. 2b.

It is important to note that the pHp values are for solutions aged for one hour (Table 1). Hayden and Rubin, like other workers, found that the precipitate will form at a lower pH as the solution is aged. For example, at 5.0×10^{-4}M the pHp is 4.70 for a solution aged 24 hours and 4.35 for one aged three months. Hayden and Rubin suggest this is due to the solution proceeding from a highly oversaturated state to a saturated or equilibrium condition.

Aluminum Sulfate

The aqueous equilibria of aluminum in a dilute aluminum sulfate solution is considerably more complicated than aluminum nitrate because of the possible formation of mixed sulfatohydroxo-aluminum complexes. In addition, it is not possible to arrive at a complete description of the aqueous equilibria

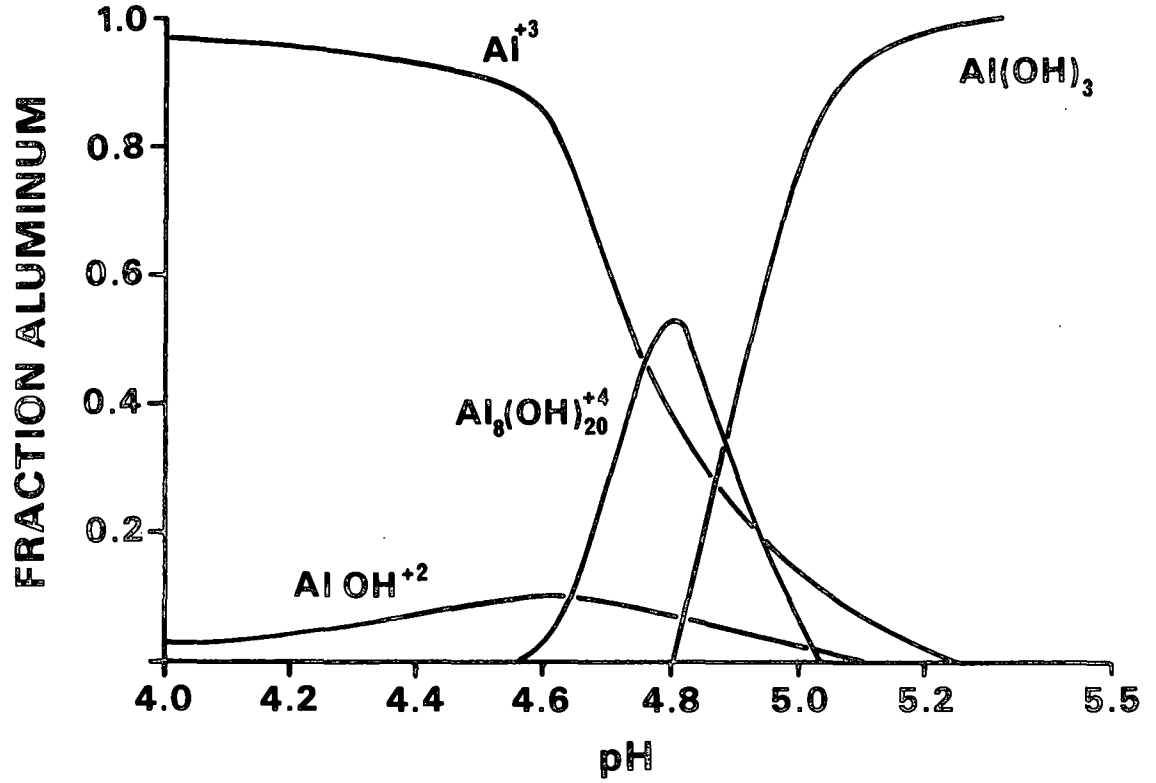

Figure 2a. Distribution of aluminum species as a function of pH for $AlCl_3$ (2.5×10^{-4} M Al).[2]

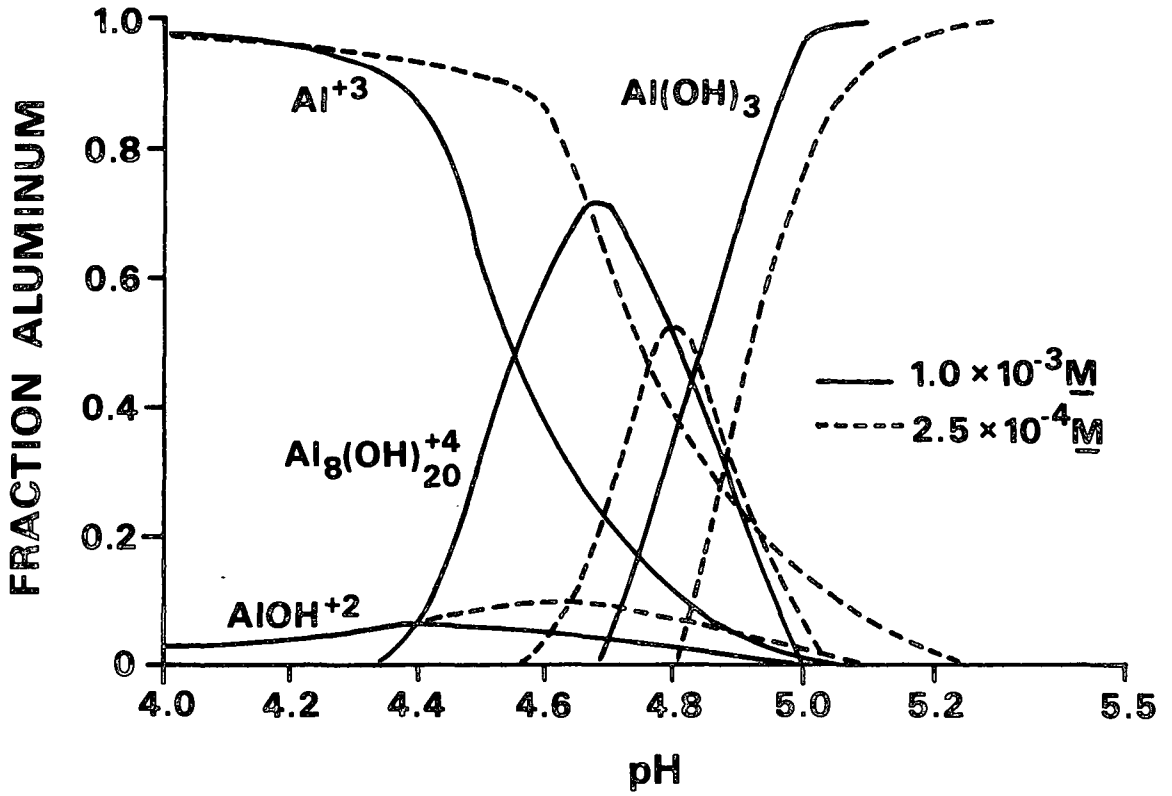

Figure 2b. Distribution of aluminum species as a function of pH and aluminum concentration for $AlCl_3$.[2]

using potentiometric analysis. In order to study metal-anion complexing by this technique, the anion must hydrolyze to a certain extent. Sulfate is not a hydrolyzing anion and, therefore, no detectable pH change would be associated with an aluminum-sulfate interaction.

A review of the literature, however, yields some likely possibilities as to the existing species. The review on sulfate-aluminum complexes can be divided into three regions: (1) below pH 4.0, (2) between 4.0 and the pHp, and (3) above the pHp (precipitation region).

Below pH 4.0, aluminum hydrolysis is considered to be insignificant so the complexing effects of the hydroxide group can be ignored. In this region, nuclear magnetic resonance (NMR),[15,16] infrared (IR),[17] and Raman[18] spectroscopy provide evidence for the formation of the $AlSO_4^+$ complex. The investigations of Stryker and Matijevic[19] and Ow[20] also provide evidence for the $AlSO_4^+$ complex in this region.

Between pH 4.0 and the pHp, hydrolysis and pHp studies by Hayden and Rubin support the presence of a soluble sulfatohydroxo-aluminum species. Specifically, their data indicated a 4+ charged polynuclear species along with a species of lower charge being formed in the region of maximum hydrolysis before the pHp.

Above the pHp, precipitatation studies by Hayden and Rubin support the presence of an insoluble sulfatohydroxo-aluminum species. They observed the addition of the sulfate ion to decrease the pHp. If the sulfate anion complexed with the aluminum and was displaced by hydroxide ions to form aluminum hydroxide, then a higher concentration of hydroxide would be required to displace the

sulfate from the soluble complex and the pHp would be shifted to a higher pH. However, the pHp was shifted to a lower pH indicating that sulfate was incorporated into the precipitate, thus requiring a lower concentration of hydroxide for precipitation.

As mentioned above, Hayden and Rubin observed the addition of sulfate ion to decrease the pHp. Their experimental values for dilute solutions of aluminum nitrate and aluminum sulfate at several aluminum concentrations are shown in Table 2.

Table 2. Effect of anion on the pH of precipitation (pHp-exp. observed pH of precipitation at one hour by Hayden and Rubin).

Aluminum Concentration, M	pHp	
	$Al(NO_3)_3$	$Al_2(SO_4)_3$
1.0×10^{-4}	4.88	4.67
2.5×10^{-4}	4.76	4.52
5.0×10^{-4}	4.66	4.41
1.0×10^{-3}	4.57	4.30

Another difference between the two aluminum salts is the effect of aging on the pHp. With aluminum nitrate Hayden and Rubin reported a reduction in the pH of precipitation (by approximately 0.35 pH unit) upon aging for three months. With age, the solutions probably proceeded from a highly oversaturated state to a saturated or equilibrium condition by the precipitation of the aluminum at a lower pH. However, for aluminum sulfate the pHp is reduced by only 0.07 pH unit upon aging. Therefore, solutions of aluminum sulfate did not appear to be as highly supersaturated.

ALUMINUM ADSORPTION ONTO CELLULOSE

Arnson's study[2] has been the most informative study on aluminum adsorption to date. His study has shown an excellent correlation between Hayden and Rubin's aluminum species distribution curves and aluminum adsorption, and he has interpreted the nature of the adsorbed aluminum. In his study, aluminum adsorption was related to the type of aluminum species by varying pH, adsorption time, aluminum concentration, and aluminum salt (Fig. 3-6, respectively).

Using Hayden and Rubin's aluminum species distribution curves, Arnson considered the adsorption of aluminum from aluminum chloride solutions in three distinct pH regions. One region was at the lower values of pH where Al^{3+} and $AlOH^{2+}$ are the only species. Another region was at the middle of the narrow pH band where the polynuclear species forms but below the pHp. Here, the aluminum species Al^{3+}, $AlOH^{2+}$, and $Al_8(OH)_{20}^{4+}$ are present, and most of the aluminum exists as Al^{3+} or $Al_8(OH)_{20}^{4+}$. The last region was above the pHp which is dominated by the formation of the colloidal aluminum precipitate.

The cellulosic substrate used in his study was a fines-free, refined cotton linters pulp. This was oxidized to a carboxyl content intermediate between a bleached kraft softwood and a bleached kraft hardwood, and had a hydrodynamic surface area typical of a moderately-beaten, classified wood fiber pulp. All experiments were conducted in a constant background ionic strength of 0.01N KCl. The following paragraphs are excerpts from Arnson's thesis[14]:

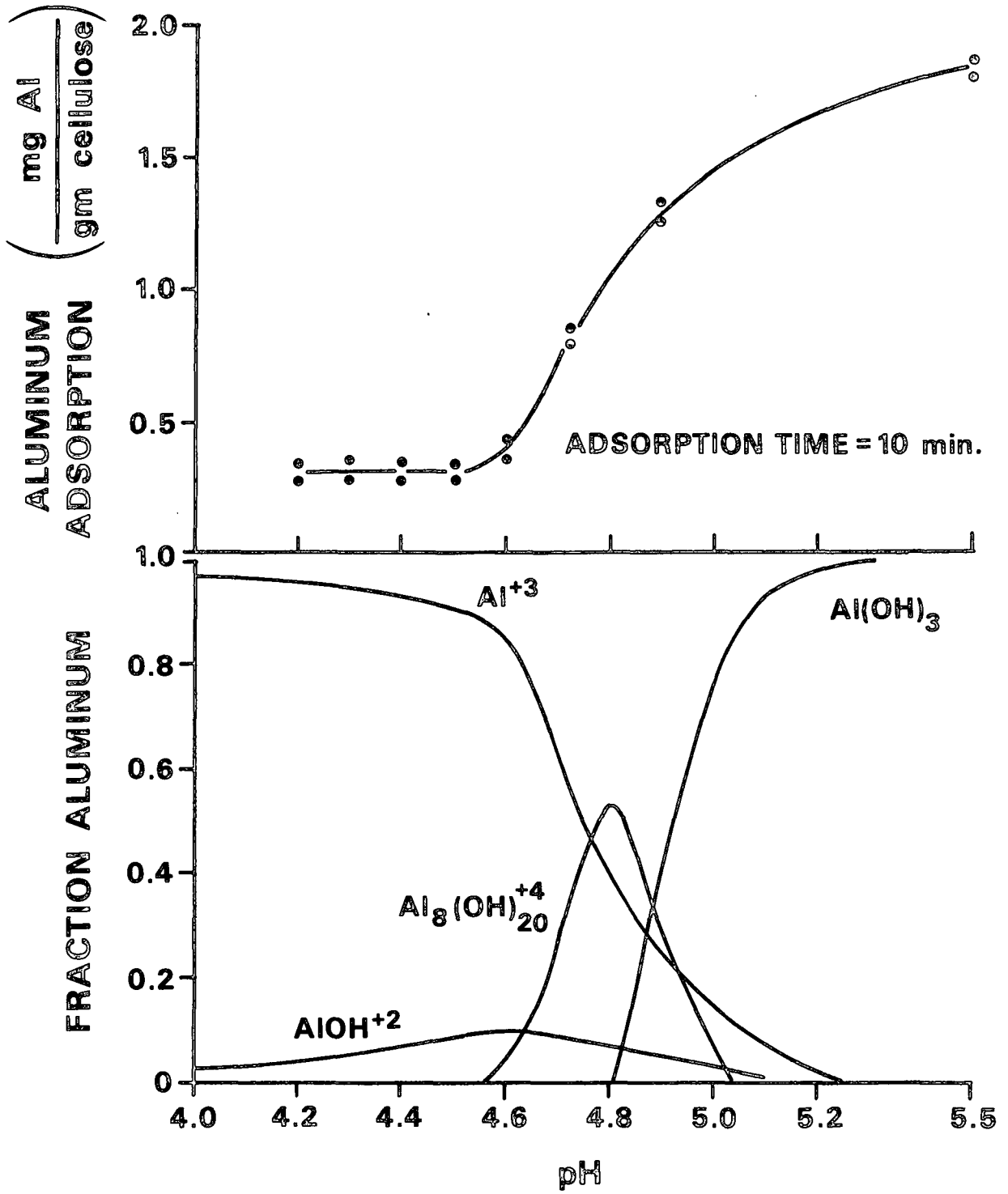

Figure 3. Top: Aluminum adsorption as a function of pH for $AlCl_3$ at 2.5×10^{-4}M Al.[2]
Bottom: Distribution of aluminum species as a function of pH for $AlCl_3$ at 2.5×10^{-4}M Al.[2]

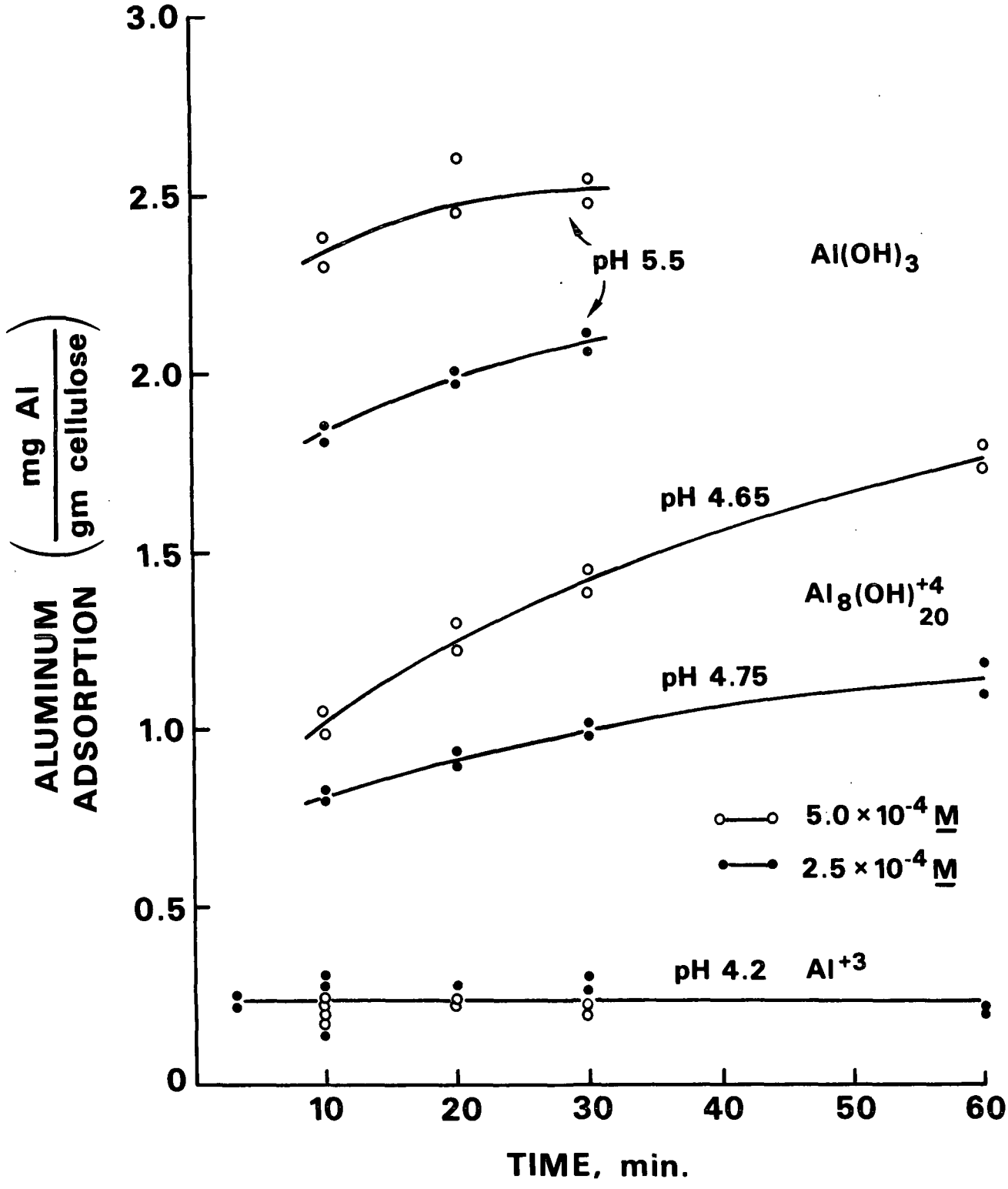

Figure 4. Aluminum adsorption as a function of pH, time, and aluminum concentration.[2]

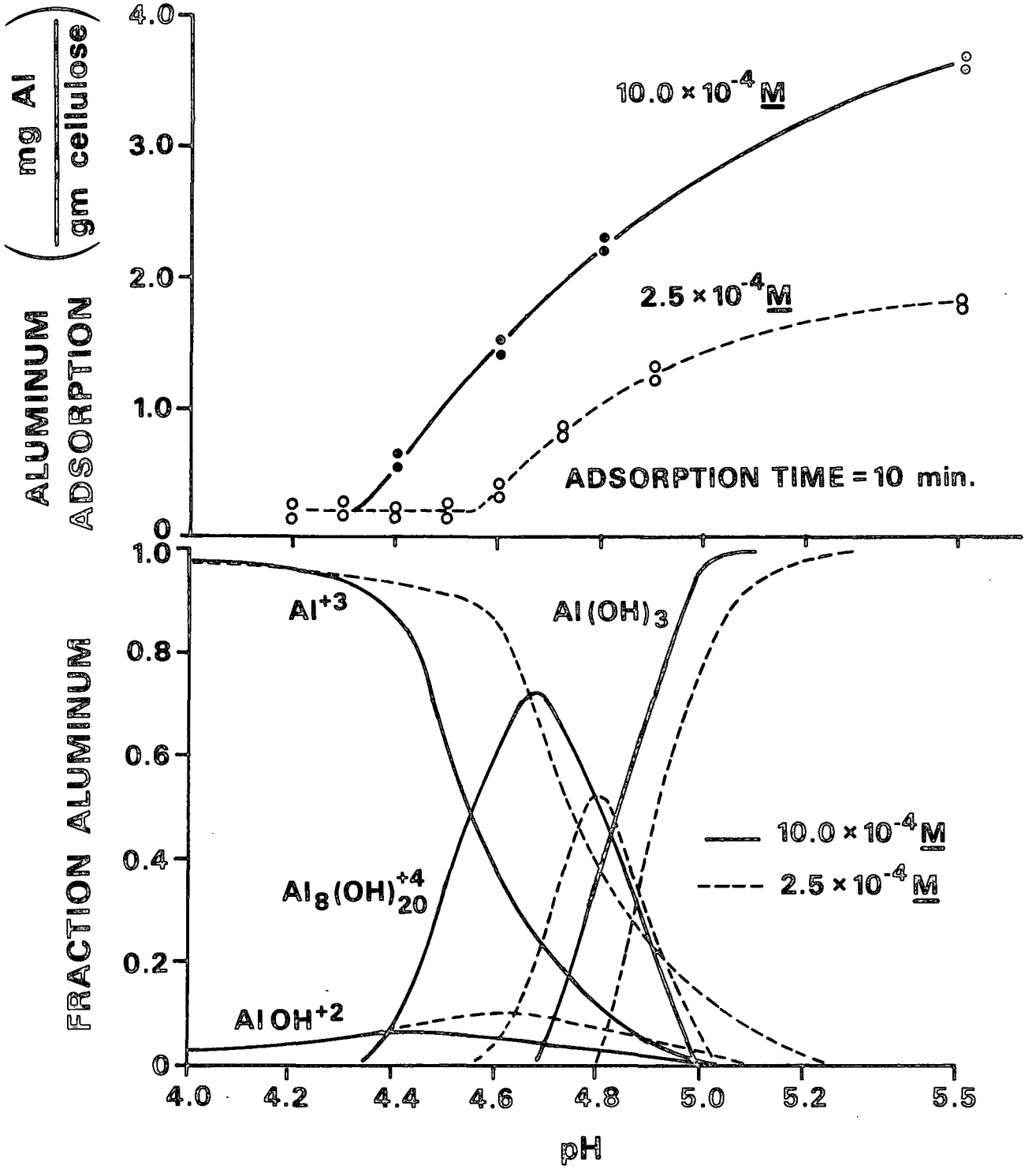

Figure 5. Top: Aluminum adsorption as a function of pH and aluminum concentration for $AlCl_3$.[2]
Bottom: Distribution of aluminum species as a function of pH and aluminum concentration for $AlCl_3$.[2]

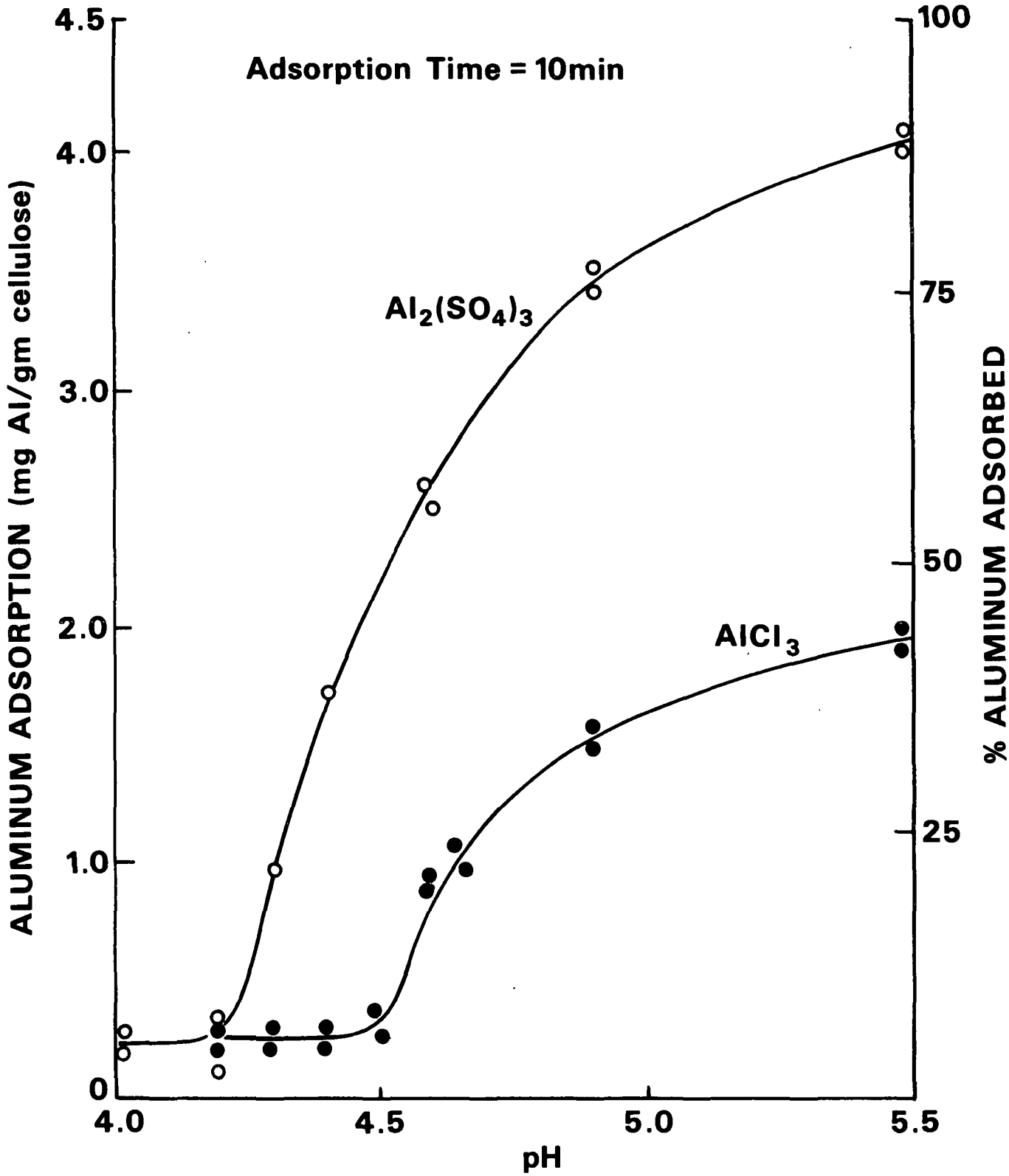

Figure 6. Comparison of aluminum adsorption for $AlCl_3$ and $Al_2(SO_4)_3$ (5.0×10^{-4} M).[2]

For each of the above pH regions the amount of adsorbed aluminum was observed to decrease significantly when the carboxyl content of the pulp was decreased. This indicated that an ion exchange mechanism with the carboxyl groups is an important aspect of the adsorption process in each of the regions.

Adsorption in the low pH region (4.0-4.5) was observed to be independent of time and aluminum concentration. The adsorption mechanism in this region was interpreted to occur by a simple and rapid ion exchange process with Al^{3+} probably being the primary aluminum species to adsorb.

The amount of adsorbed aluminum in the intermediate pH region (4.4-4.8) was greater than in the low pH region. It was observed to be dependent on both time and aluminum concentration. The adsorption mechanism in this region was also interpreted to occur primarily through an ion exchange process. Here, $Al_8(OH)_{20}^{4+}$ and Al^{3+} are the primary aluminum species to adsorb. The observed concentration and time dependency was proposed to be the result of the continued formation and adsorption of the polynuclear species.

The highest levels of adsorbed aluminum were found to occur in the high pH region (4.7-5.5). The positively-charged aluminum hydroxide precipitate was believed to be the principal aluminum species adsorbed by the fibers in this region. The mechanism by which the precipitate adsorbs onto cellulosic fibers was not determined, but it was found that electrostatic interactions, between the precipitate and the fiber and laterally between the precipitate particles, are important elements of the adsorption process in this region.

The adsorption behavior of aluminum from a dilute solution of aluminum sulfate was found to be predictable and quite analogous to the adsorption pattern for aluminum chloride with the characteristic sharp increase in adsorption

occurring between pH 4-5. The only observed differences in adsorption between the two salts were that the aluminum sulfate curve broke upward at 0.25-0.30 pH units lower than for aluminum chloride, and the amount of adsorbed aluminum was greater for aluminum sulfate in the high pH region where the precipitate is formed. The observed differences could be explained by known differences in their aqueous solution properties. It was concluded that the adsorption of aluminum from aluminum sulfate solutions was controlled by adsorption mechanisms similar to those occurring in aluminum chloride solutions, although the exact composition of the polynuclear species was not known.

CATIONIC POLYELECTROLYTE ADSORPTION

Under equilibrium conditions and at low additions, the adsorption of cationic polyelectrolytes onto anionic surfaces is fairly complete. However, as the addition is increased, the polymer adsorption will approach a limit corresponding approximately to a "monolayer" saturation level. This has been inferred from adsorption isotherms on cellulosic materials[21,22] and other anionic particles.[23-28] At the saturation level the lateral interactions between adsorbed polymer chains prevent further adsorption and the zeta potential is quite positive.[22,29]

In papermaking systems, the potential for a nonequilibrium situation exists. Cationic polyelectrolytes used as retention aids in a polyelectrolyte system are generally added to the stock just after the fan pump somewhere near the final forming area.[30] The polymer's total retention time in the papermaking system is typically less than a minute.[31] A nonequilibrium situation may be especially likely in an alum-cationic polyelectrolyte papermaking system because of the potential competition between alum and the polymer for adsorption sites on the surface of the particles in the furnish.

The mechanism by which cationic polyelectrolytes are adsorbed onto the cellulose fiber's surface appears to be dual in nature.[32,33] The primary adsorption comes from the direct ionic bond formation between the dissociated carboxyl groups and the polyelectrolyte. This is accomplished by an ion-exchange mechanism where a simple electrolyte is displaced from a carboxyl group on the fiber surface by the cationic polyelectrolyte, which in turn forms an ionic bond with the carboxyl group. The secondary adsorption takes place via hydrogen bonding or Van der Waals forces.

In an alum-cationic polyelectrolyte system the above mechanism may be further complicated. Moore[34] has proposed that a cationic polyelectrolyte can also adsorb through polymer-sulfate anion-hydroxyaluminum bridging. Basically, it is the same as polymer bridging except that the polyelectrolyte attaches to the sulfate ion in the hydroxyaluminum complex which is on the fiber surface, rather than attaching directly to the fiber.

PRESENTATION OF PROBLEM AND THESIS OBJECTIVES

Alum (aluminum sulfate) is a common wet-end additive which is known to have differing effects on the retention in papermaking systems using cationic polyelectrolytes as retention aids. The differing effects of alum on retention must be due to either differing materials and/or conditions. Prior studies have shown that under differing conditions of pH and alum concentration alum forms various species with differing adsorption properties.[2] Since cationic polyelectrolytes, like alum, must also adsorb onto negative surface sites on the fiber surface, there may be interactions between the two adsorbing additives. Any interaction between alum and a cationic polyelectrolyte will likely be a function of the various aluminum species. This may explain the differing effects of alum on retention with a cationic polyelectrolyte.

Unfortunately, the aqueous chemistry of alum is not well defined. Hayden and Rubin[1] have defined the aqueous chemistry of aluminum chloride using potentiometric and precipitation analyses. However, alum contains a complexing anion (sulfate), and to study metal ion-anion complexing the anion must hydrolyze to a certain extent. Sulfate is not a hydrolyzing anion and, therefore, it is not possible to investigate alum's aqueous chemistry using potentiometric analysis. Nevertheless, an adsorption study by Arnson[2] has shown similarities between alum and aluminum chloride, suggesting that their aqueous chemistry is probably quite similar. Therefore, any study on alum should include aluminum chloride, due to the well-defined chemistry of aluminum chloride.

Interaction between alum and cationic polyelectrolytes will also likely be a function of polymer concentration and polymer adsorption time.

Since both additives are cationic and must adsorb onto negative sites on the fiber surface to function, interactions may include competition for the fiber surface. Therefore, besides alum species and alum concentration, competition will also likely be a function of polymer concentration and polymer adsorption time.

It can be hypothesized from the preceding paragraphs that (1) alum can affect the adsorption of a cationic polyelectrolyte, (2) the influence of alum on polyelectrolyte adsorption varies when altering the pH and aluminum concentration due to the formation of differing aluminum species possessing differing properties, (3) polyelectrolyte adsorption in the presence of alum will also be a function of polyelectrolyte concentration and polyelectrolyte adsorption time, and (4) a study including aluminum chloride, with its better defined chemistry, can enhance the understanding of alum's role in affecting the adsorption of a cationic polyelectrolyte.

With the above hypothesis in mind, the specific objectives of this thesis were

1. to determine whether aluminum salts (i.e., aluminum chloride and aluminum sulfate) can influence the amount of adsorbed cationic polyelectrolyte,
2. to establish under what conditions of pH, aluminum concentration, aluminum salt, polymer concentration, and polymer contact time this influence can occur, and
3. to determine the mechanism(s) by which the aluminum salts influence the amount of adsorbed polyelectrolyte.

GENERAL APPROACH

Proper analysis of an adsorption process requires experimental data from a well-characterized system both with respect to the adsorbent and the adsorbate. As in Arnson's study, the absorbent was a fines-free, oxidized cellulosic fiber produced from a commercial cotton linters pulp. Aluminum chloride, aluminum sulfate, and a ^{14}C tagged cationic polyelectrolyte were used as the adsorbates. The Hayden and Rubin solution of the aqueous equilibria was used to interpret the actual form of the aluminum ion in solution.

Many of the past studies involving aluminum adsorption by cellulosic fibers are characterized by a lack of systematic investigation with regard to pH control. From the work of Hayden and Rubin and other workers, it is evident that the pH and aluminum concentration of the system must be controlled independently of each other because of the complicated aqueous chemistry. As in Arnson's study, the importance of good pH and aluminum concentration control has been emphasized throughout the experimental program.

Keeping the above criteria and the objectives in mind, the experimental program was conducted in a systematic manner to determine the effect of aluminum salts on the adsorption of the cationic polyelectrolyte. The experimental program was divided into six sections:

1. Characterization of the materials
2. Aluminum adsorption
3. Polymer adsorption
4. Influence of polymer on aluminum adsorption
5. Influence of aluminum on polymer adsorption
6. Investigation of mechanisms

To investigate the interactions between aluminum and polymer adsorption, comparative adsorption studies were conducted. Aluminum adsorption in the system without polymer and polymer adsorption in the system without aluminum were used as references to measure how the two additives alter the adsorption behavior of one another.

The approach to investigating the mechanisms needs more explanation. To determine the mechanisms by which aluminum salts influence polymer adsorption, the various possibilities and their characteristics had to be rationalized. The mechanisms by which aluminum salts affect polymer adsorption may function on the surface of the cellulose or in solution. If the mechanisms function on the surface of the cellulose, then it is important to understand how the polymer adsorbs. It may adsorb (1) directly onto carboxylate groups after the displacement of the previously adsorbed aluminum (or other cation) and/or (2) onto the previously adsorbed aluminum species, possibly through polymer-sulfate ion-hydroxyaluminum-cellulose bridging. Only the first mechanism involves competition for the cellulose surface. However, if the mechanism(s) by which aluminum salts affect polymer adsorption function in solution, then it is important to examine the aqueous species which may interact with the polymer. In solution it is unlikely that the cationic aluminum species will interact with the cationic polymer. However, aluminum salts contain anions, and anions are known to function as counterions and screen the charges of cationic polymers. This mechanism would reduce the "effective" charge of the polymer, thus reducing both the molecular size of the polymer in solution (i.e., the radius of gyration*) and the electrostatic attraction between the cationic polymer and the

*Radius of gyration - the root-mean-square distance of the monomers of the chain from its center of gravity, $\langle S^2 \rangle^{1/2}$.

anionic fiber surface. The multivalent sulfate anion would be more effective than the monovalent chloride ion under this mechanism.

In summary, the ways in which aluminum salts may affect the adsorption of a cationic polyelectrolyte are by (1) competition for the cellulose surface, (2) polymer-multivalent anion-hydroxyaluminum-cellulose bridging, and (3) polyelectrolyte charge reduction by anions.

Characteristics of each mechanism were then rationalized. Characteristics of the first mechanism may include (1) an inverse relationship between aluminum adsorption and polymer adsorption, (2) displacement of the previously adsorbed aluminum by polymer, and (3) reduction in polymer adsorption with increasingly positive fiber charge.

Characteristics of the second mechanism may include (1) a direct relationship between aluminum adsorption and polymer adsorption, (2) adsorption of polymer onto previously adsorbed aluminum, and (3) dependence of polymer adsorption on valence of anion.

A characteristic of the third mechanism may be a decrease in polymer adsorption, due to a lower adsorption rate, with increasing valence and concentration of anions.

Various experiments were examined for the above characteristics. These included

1. Comparative adsorption studies
2. Fiber charge analysis
3. Aluminum desorption experiments (i.e., the investigation of polymer adsorption onto previously adsorbed aluminum)

4. Aluminum sulfate precipitate analysis (for sulfate content)

5. Effect of anion valence and concentration on polymer adsorption

6. Effect of cation valence and concentration on polymer adsorption (discussed later).

EXPERIMENTAL

MATERIALS

Cellulosic Fibers

Cotton linters fibers from Arnson's study[2] were selected as the cellulosic substrate. Arnson chose cotton linters for several reasons. First, cotton linters are similar to wood fibers in that both consist of a primary wall of low cellulose content, a secondary wall of high cellulose content, and a lumen containing protoplasmic residues. Second, although more difficult to refine, cotton linters develop a similar surface of high cellulose content once the primary wall has been removed. Finally, unlike wood fibers, cotton linters are practically free of any lignin or hemicelluloses.[35,36] Thus, a refined, fines-free cotton linters pulp should potentially serve as a good model of the fiber portion of a papermaking furnish. There should be no interference of the fines, soluble lignin, or hemicelluloses on the adsorption of aluminum salts and cationic polyelectrolyte onto the surface of the fibers.

The carboxyl content of cotton linters is, unfortunately, significantly lower than wood fiber. Since the carboxyl groups are believed to be the primary adsorption sites, Arnson found it necessary to oxidize the cotton linters. He used a mild, two-step process of potassium dichromate/acidified sodium chlorite for the oxidation. This process has previously been used by Luner and coworkers[37,38] to oxidize rayon, cotton linters, and wood fibers.

With the preceding rationale in mind, Arnson treated a commercial grade of papermaking cotton linters in the following manner to yield the cellulosic substrate for our investigations: (1) refined to 250 mL CSF, (2)

classified with two passes over The Institute of Paper Chemistry's web former, (3) extracted with benzene:ethanol (1:1), (4) oxidized by the above-mentioned, two-step process, and (5) washed, air dried, and stored in polyethylene bags without a preservative. The characteristic properties of the cotton linters pulp are presented in Table 3.

Table 3. Characteristic properties of the cotton linters pulp. (Data experimentally determined by Arnson.)

Fiber length - arithmetic average	1.2 mm
- weighted average	1.5 mm
Hydrodynamic specific surface area	10,400 cm^2/g ± 2%
Hydrodynamic specific volume	1.99 cm^3/g ± 4%
Carboxyl content	5.0 meq/100 g ± 8%
Ionization at pH 4.0 in 0.01N KCl	80%
Ionization at pH 5.0 in 0.01N KCl	90%

The fiber length is approximately the same as most hardwood species;[39] the specific surface area corresponds to a moderately-beaten, classified wood fiber pulp;[40] the carboxyl content is intermediate between bleached kraft softwoods at 3.5-4.0 meq/100 g[41-43] and bleached kraft hardwoods at 6.0-9.0 meq/100 g.[43] General considerations of the pulp properties suggest that the cotton linters pulp represents a fairly good model for the long fiber fraction of a fine papers furnish. A complete description of the original cotton linters, each treatment, and the characterization procedures is presented in Arnson's thesis.[14]

Aluminum Salts

As in Arnson's study, stock solutions (~ 0.3M) of aluminum chloride ($AlCl_3 \cdot 6H_2O$) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) were prepared from analytical reagent grade chemicals and filtered through a Millipore filter (0.22 μm pore diameter). The aluminum content of the stock solutions was determined gravimetrically by reacting the aluminum with the organic chelate, 8-hydroxyquinoline, to form the insoluble, aluminum oxinate.[44] A relative error of 0.4% was observed in the determination of aluminum content using this method. Dilute aluminum solutions were freshly prepared from the stock solution just prior to use for a set of adsorption experiments.

Cationic Polyelectrolyte

The cationic polyelectrolyte used in this study was a high molecular weight, low-charge density polyacrylamide. This type of polymer is representative of the majority of the cationic retention aids used in the paper industry.[30] The synthesis of the polyelectrolyte involved the free radical copolymerization of dimethylaminopropyl methacrylamide and acrylamide, followed by the quaternization of the tertiary amine groups with methyl iodide. The polymer was tagged with ^{14}C labeled methyl iodide in order to follow its adsorption onto cellulose. A complete description of its synthesis is presented in Appendix I.

Characterization of the Polyelectrolyte

The ^{14}C labeled copolymer was characterized by charge, molecular weight, and radioactivity.

Charge Analysis (Net)

The net charge on the polyelectrolyte was determined by a spectrophotometric method using a cationic dye and an anionic polymer. The method, which

was developed for this thesis, is similar in principle to that of other methods[45,46] involving other reagents. The method works on the principle that a cationic polymer can displace a cationic dye from an anionic polymer. Therefore, if a dye-anionic polymer complex is added to a known concentration of cationic polymer, the dye is released from the anionic polymer in the amount corresponding to the cationic polymer's charge. This would yield the net charge of the cationic polymer if the uncomplexed dye can be distinguished from the complexed dye. By choosing a dye whose absorbance changes upon being released by the anionic polymer, it was possible to measure the displacement of the dye and hence determine the charge density of the cationic polymer. A complete description of the procedure is presented in Appendix II.

Charge Analysis (Negative)

The anionic charge on the cationic polyelectrolyte (i.e., degree of hydrolysis) was determined by potentiometric titration. Commercial polymers typically possess some degree of hydrolysis, which is usually small compared with the cationic charge. For the tagged polymer this was determined by potentiometric titration of the polymer solution. Hydrolysis of the polymer during preparation and/or storage results in the formation of carboxyl groups in the form of acrylic acid. Since the pKa of acrylic acid is 4.25, solutions of the hydrolyzed polymers are buffered around pH 3.5 to 5.5. Therefore, the degree of hydrolysis can be determined by comparing the degree of buffering of a polymer solution to that of distilled water using potentiometric titrations. A complete description of the procedure along with the results is presented in Appendix III.

Molecular Weight Analysis

The molecular weight of the polymer was determined by viscosity measurements using a Ubbelohde viscometer. The reduced viscosity was determined at several concentrations. By extrapolation to zero concentration, the intrinsic viscosity was determined. Using relationships by Francois, et al.[47] and Klein, et al.,[48] it was possible to relate the intrinsic viscosity to the molecular weight. Details of the analysis are presented in Appendix IV.

Radioactivity Analysis

The radioactivity of the polymer was determined by liquid scintillation counting. A known concentration of the polymer was mixed with a liquid scintillation cocktail (Aquascint-ICN) and counted on a Beckman LS-100 liquid scintillation counter.

APPARATUS

The experimental apparatus used to study the adsorption of aluminum and polymer by cellulosic fibers is shown in Fig. 7 and 8. It should be noted that low-surface energy materials (polypropylene, Teflon, and polyvinyl chloride) and treated glassware are used wherever possible in order to minimize the loss of aluminum and polymer onto nonfibrous surfaces.

Figure 7 shows the apparatus used to maintain the proper pH conditions and mixing during aluminum adsorption, prior to polymer adsorption. During a run, the furnish was stirred at a moderate rate, sufficient to prevent the fibers from settling. A Corning Model 12 Research pH meter, readable to 0.001 pH unit, was used to monitor the pH. The electrodes were a Corning Calomel "very stable" Reference electrode and a Corning General Purpose pH electrode. As required, dilute NaOH was added from a calibrated buret (50 mL).

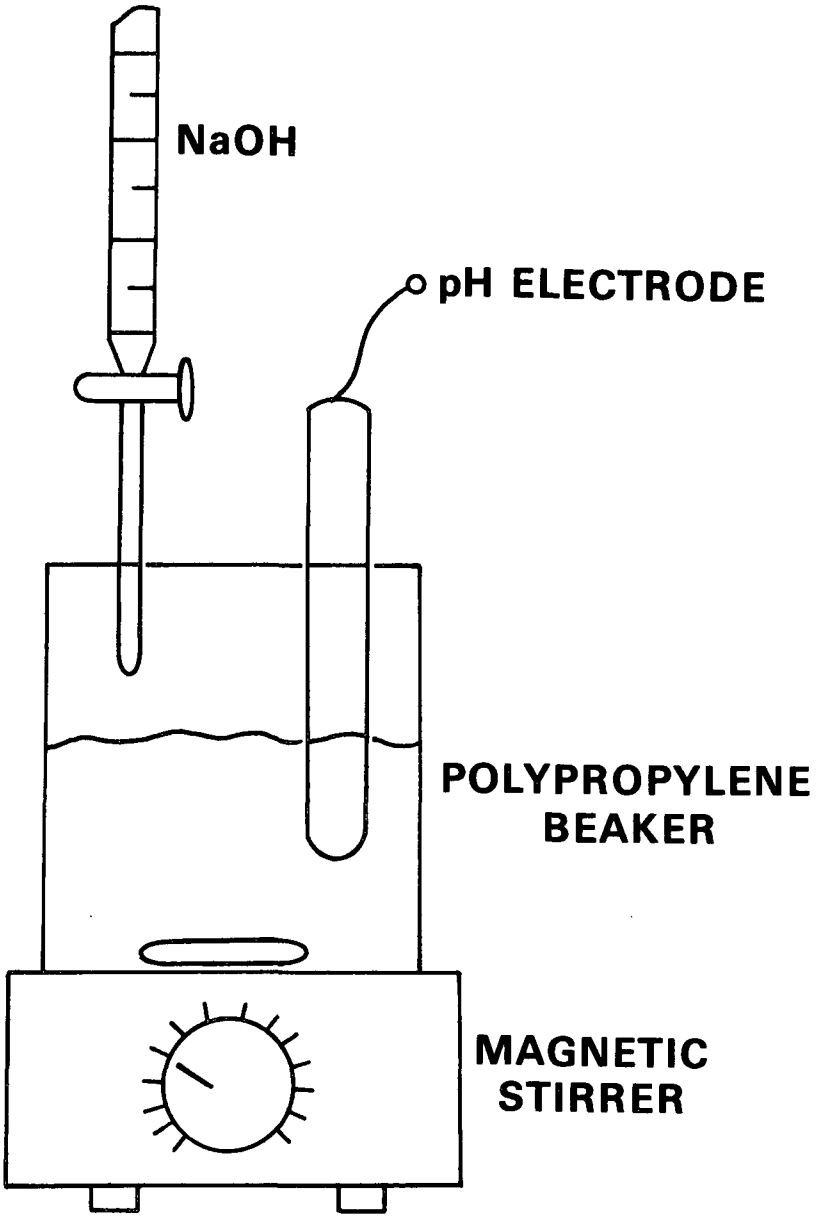

Figure 7. Aluminum adsorption apparatus (schematic).

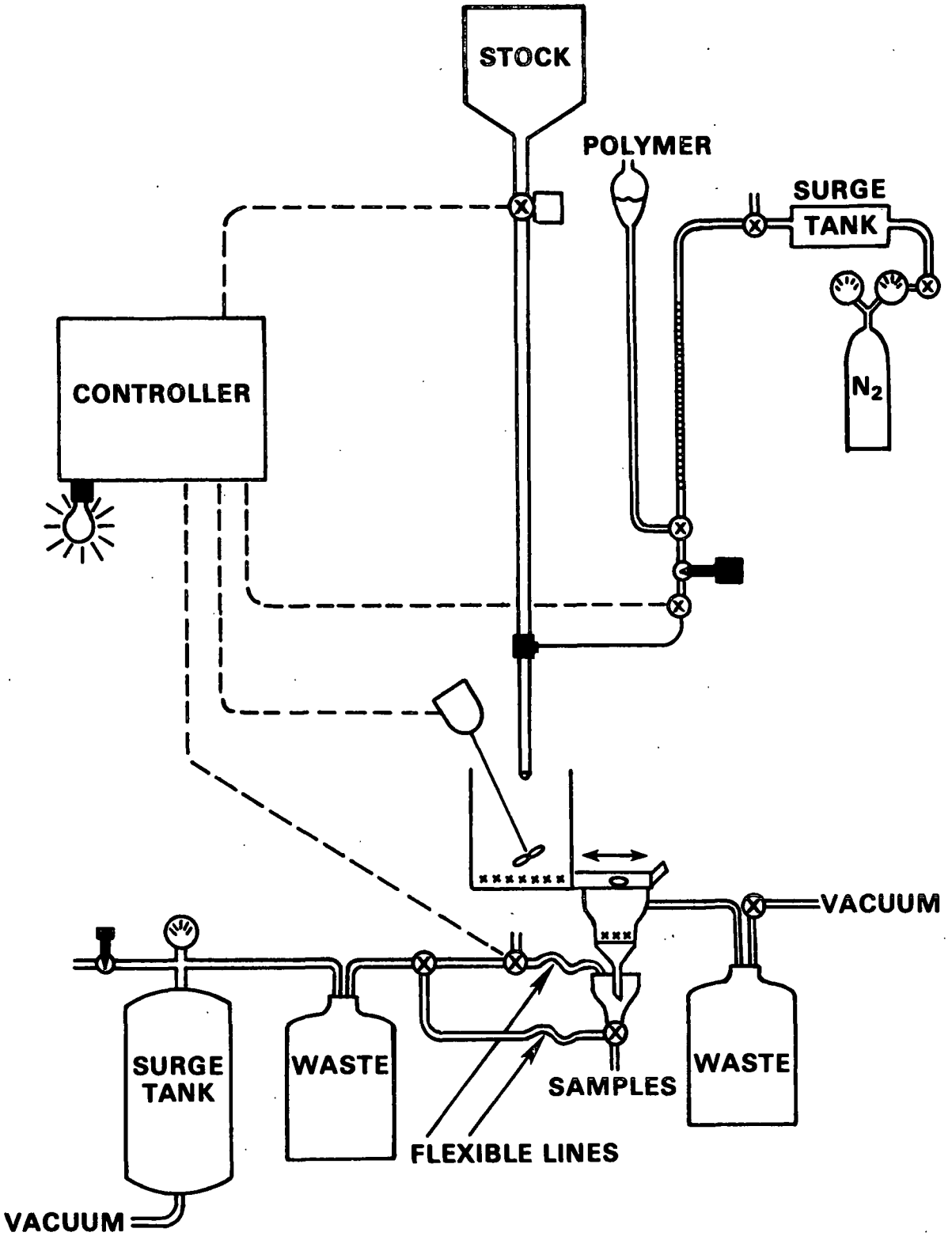

Figure 8. Experimental apparatus for polymer adsorption and separation of unadsorbed additives (schematic).

Figure 8 shows the apparatus used to add the polymer to the pulp and to separate the unadsorbed aluminum and polymer from the pulp, while simulating the real aspects of a papermaking system. This apparatus was constructed by Arnson,[49] but modified for use in this study. The apparatus consists basically of a (1) pulp delivery section, (2) polymer delivery section, (3) rapid mixing tee, (4) drainage jar, (5) sampling and cleaning section, and (6) controller.

The pulp delivery section was designed to deliver the pulp to the mixing tee at a high enough velocity to achieve and maintain a well-dispersed state. This state corresponds to the damped turbulence region for fiber suspensions. The pulp delivery section consists of a holding tank, a controlled air operated valve, and a PVC line of sufficient length (45 in.) and diameter (0.50 in.) to insure turbulence in a gravity fed 0.3% consistency fiber suspension.[50]

The polymer delivery section was designed to deliver a given amount of polymer throughout the pulp plug as it flows into the drainage jar. It consists of the polymer reservoir, the graduated pipette to measure the polymer addition, a needle valve to regulate the polymer addition, a controlled solenoid valve to time the injection to coincide with the passage of the pulp plug through the mixing tee, and a constant nitrogen pressure head to supply the driving force. The proper opening and closing of the solenoid valve is important for delivery of polymer throughout the full length of the pulp plug. The operation of the solenoid valve is controlled by timers in the controller. A combination of TI photodiode-LED sensors on the pulp delivery line was used by Arnson[51] to determine the settings for the timers. To eliminate loss of the tagged polymer, all glass surfaces in contact with the polymer were pretreated with a high charge, high molecular weight, cationic polyelectrolyte.

The mixing tee was designed for rapid uniform mixing (Fig. 9). A 0.2% polymer solution was injected upstream against the pulp flow from a series of holes in the polymer delivery line which transverses the full diameter of the pulp delivery line. To insure turbulent flow and rapid uniform mixing in the pulp line, sets of rods were positioned across the pulp flow immediately above and below the polymer injection point.

A modified dynamic drainage jar was used to provide additional mixing and adsorption under turbulent conditions. The jar features (1) a polypropylene coated propeller and shaft, a polyvinyl chloride wall, and a plastic 120 mesh screen to minimize polymer loss, (2) a polyvinyl chloride baffle to improve mixing, (3) a sliding gate below the screen to prevent any filtrate from passing the screen until the desired time, and (4) a hinged bottom to allow easy access to the fiber pad after the vacuum removal of the excess water.

The sampling and cleaning section was designed for quick and easy sampling and cleaning without spillage of radioactive filtrate. It consists of (1) a filter holder containing a 10 μm pore size polycarbonate filter (Nuclepore No. 111115) to separate fines from the unadsorbed additives, (2) a constant vacuum line (25 psig) to provide fast reproducible filtration through the polycarbonate filter, (3) a controlled solenoid valve to activate the constant vacuum line, (4) a graduated receiving vessel under the filter for filtration of fixed amounts of filtrate, and (5) waste containers for the excess filtrate during testing and cleaning. The filter holder was constructed from polyvinyl chloride, the receiving vessel was polypropylene, and the support screen for the polycarbonate filter was Teflon coated.

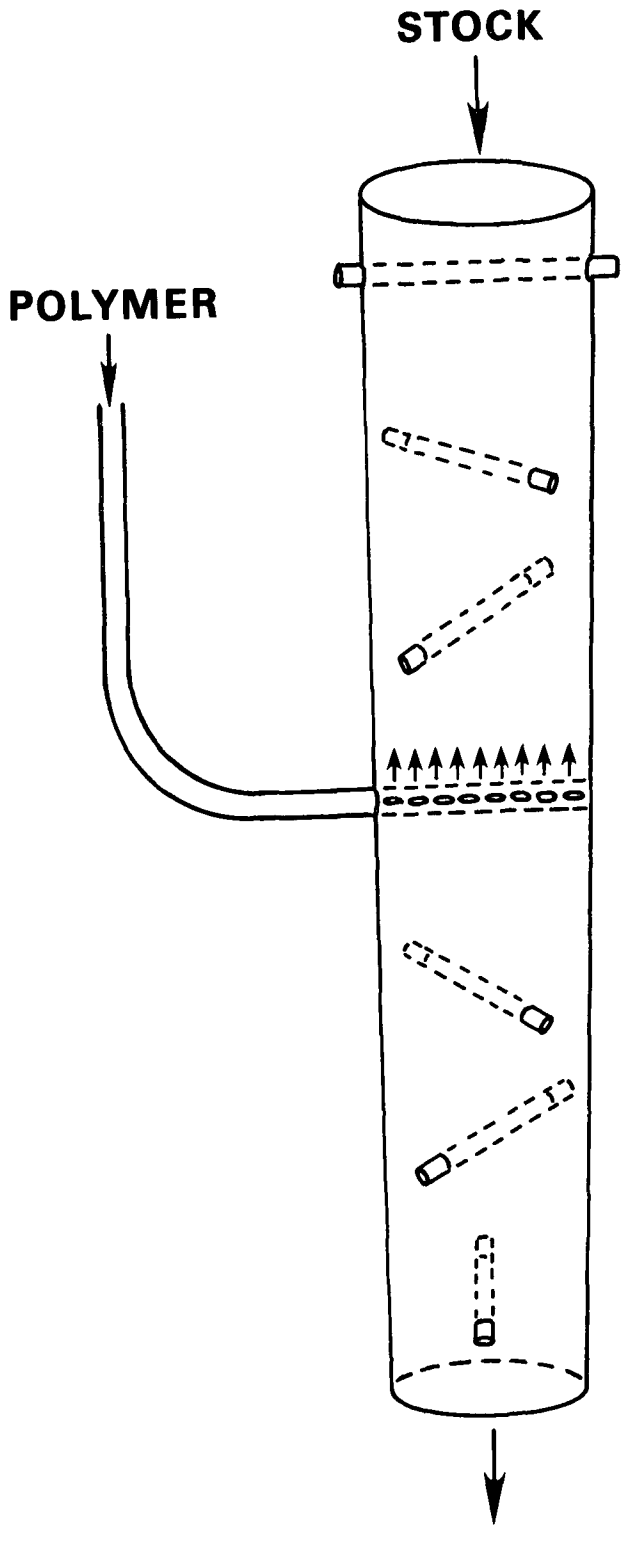

Figure 9. Schematic of the rapid mixing tee.

The controller was designed to automate the sections of the apparatus. It consisted of five timers. The first timer opened the pulp line and then closed the line after a set time (~ 10 seconds). The next two timers opened the polymer line when the leading edge of the pulp flow reached the mixing tee and then closed the polymer line when the trailing edge passed the tee. The fourth timer started the stirrer in the dynamic drainage jar immediately after the pulp started flowing in. The fifth timer activated a light, indicating when to manually open the gate, and supplied vacuum to the filter holder to pull filtrate through the polycarbonate filter. No vacuum was supplied to the dynamic drainage jar during sampling.

PROCEDURES

Ionic Strength Adjustment

As in Arnson's study[2] an ionic strength background of 0.01N KCl was used in the adsorption tests. When investigating the effect of aluminum concentration (2.5×10^{-4} to 10.0×10^{-4}M) at constant pH, there is an effect on the ionization of the carboxyl groups due to variations in ionic strength.[52,53] However, 0.01N KCl is sufficient to eliminate the influence of ionic strength on the ionization of the substrate,[53] without dominating the adsorption behavior of the system. As an aside, 0.01N KCl has a specific conductance of about 1400 μmhos/cm which is in the range of many paper mill white waters.

Adsorption Run

As in Arnson's study, all adsorption runs were done in a systematic manner with respect to the order of addition of the additives and the pH control of the system. This is essential for proper interpretation of the aluminum species that are being formed and to guard against the premature formation of aluminum precipitate. The following series of steps was maintained for each adsorption run.

A volume of dispersed pulp (440 to 460 mL) containing 1.5 g dry fiber was placed into the polypropylene beaker. The KCl (25 mL of 7.82 g/L K^+) was added next and then the pH was adjusted to 4.0 with HCl (0.1N). This was followed by the addition of the aluminum salt (5 mL) from the dilute stock solution. The remaining fluid volume (10 to 30 mL) was made up with a combination of dilute NaOH and water. The concentrations of the pulp, KCl, and aluminum previously added reach their desired concentration when the final volume reaches 500 mL.

The pH was adjusted from 4.0 to the desired adsorption pH with the addition of the dilute NaOH (0.05N). The adsorption time was started once the desired pH was initially reached. If necessary, additional NaOH was added throughout the run in order to maintain the desired pH within 0.05 pH unit. The remainder of the fluid volume was then made up with water.

After reacting in the beaker for a set adsorption time (10 min), the stock was placed in the holding tank (Fig. 8). A switch on the controller was immediately thrown, allowing the air-operated valve to open and the stock to flow down the pulp delivery line to the mixing tee. As the pulp flowed past the tee, the controller signaled the solenoid valve in the polymer delivery line to open. The stirrer in the dynamic drainage jar was then started by the controller and the polymer was allowed to adsorb under turbulent conditions for a set time (15 sec at 1200 rpm or 10 min at 150 rpm). The controller light then signaled the operator to partially open the gate for a period of approximately four seconds. The gate was then manually closed and the controller activated the constant vacuum line. A predetermined amount of filtrate (25-45 mL) was then filtered through the polycarbonate filter. At this time the controller was turned off, which opened the vacuum line to atmospheric pressure. The receiving

vessel containing the unsorbed additives was then drained through a stopcock into a polypropylene beaker for subsequent aluminum and polymer analysis. The other vacuum line and the gate were then both opened to remove the remaining fluid from the jar. The bottom of the jar was then swung back on its hinge for removal of the fiber pad for drying and weighing.

Cleaning of the apparatus was then accomplished by repeating the operations described in the last paragraph with distilled water in place of the pulp and with the polymer delivery line closed.

After the sample analysis, the amount of adsorbed aluminum or polymer was calculated from the following relationship and was expressed on a weight/weight basis.

$$A = \frac{(C_i - C_f)V}{M} \qquad (1)$$

where A = adsorbed additive (aluminum or polymer), mg/g cellulose

C_i = initial concentration of additive, ppm

C_f = concentration of additive in filtrate, ppm

V = total volume of solution, L

M = mass of cotton linters pulp, g

Aluminum Analysis

The method for aluminum detection was developed by modifying a published procedure[54] for the analysis of trace quantities of aluminum. In the published procedure, the aluminum in an aqueous sample was chelated with 8-hydroxyquinoline at pH 8.0 (NH_4OH/NH_4Ac buffer) and extracted with methyl isobutyl ketone. The quantity of ketone is small compared with the volume of the aqueous sample, thus resulting in an increased concentration of aluminum in the

ketone layer. The ketone layer is then analyzed for aluminum by atomic absorption spectroscopy.

For ease and precision, the above procedure was modified. It was observed in the above procedure that the extracted aluminum was strongly colored in the yellow region. The color appeared proportional to the concentration of aluminum in the samples. Therefore, an effort was made to analyze the samples on a Perkin-Elmer UV-visible range spectrophotometer (Model 320). With a 1-cm cell at 450 nm, the concentration was linearly related to the absorbance. This method gave approximately a 0.1 ppm sensitivity (3.0% error at the lowest aluminum concentration, 2.5×10^{-4}M aluminum), produced no drift with time, and was much simpler than the atomic absorption procedure to conduct. A complete description of the procedure is presented in Appendix V.

Polymer Analysis

The polymer concentration was determined by liquid scintillation counting. Four milliliters of a sample of unknown concentration was mixed with 10 mL of a liquid scintillation cocktail (Aquascint-ICN) and counted on a Beckman LS-100 liquid scintillation counter. The samples were related to standard samples to obtain the concentration in ppm. The method gave approximately a 2% variability.

pHp Determination

Due to the absence of information in the literature, the effect of fibers on the pH at which aluminum starts to precipitate (pHp) was determined. Hayden and Rubin[1] have already determined the pHp values for aluminum sulfate and aluminum chloride in the absence of fibers. As in Hayden and Rubin's study, light scattering measurements were used. A Perkin-Elmer 650-10S fluorescence spectrophotometer was used to conduct the light scattering measurements. The

wavelength used was 400 ± 2 nm. The accuracy of the method was checked by determining the pHp values in the absence of pulp and comparing these values to Hayden and Rubin's. Values for the pHp, in the presence of pulp, were determined by light scattering measurements on the filtrate samples from aluminum adsorption runs at various pH's, above and below the pHp. The effect of fines on the light scattering measurements was determined by acidification of the filtrate samples, which removes the aluminum precipitate. Corrected light scattering values were then interpolated in order to obtain accurate values for the pHp's. This method had a sensitivity of approximately 0.05 pH unit at 10.0 x 10^{-4}M aluminum chloride.

Zeta Potential Analysis

Zeta potential was used as a measure of fiber charge. Measurements were conducted on selected filtrate samples from the adsorption runs. Samples were removed from the dynamic drainage jar filtrates prior to the filtration through polycarbonate filters. Due to incomplete classification of the cotton linters during preparation, enough fines were present to conduct the analyses. A Model B Zeta Meter (Zeta Meter Inc.) was used for the electrophoresis measurements.

Aluminum Sulfate Precipitate Analysis

Precipitate formed in a 4.0 x 10^{-4}M aluminum solution at pH 5.5 was isolated and analyzed for aluminum and sulfate content. The precipitate was isolated by adsorption onto cotton linters according to the standard adsorption run procedure. After complete drainage of the dynamic drainage jar, 500 mL acidified water (0.002N HCl) was added to desorb the precipitate (pH 3.0). After desorption, the acidified water was drained and analyzed for aluminum and sulfate content. Ion chromatography was used to analyze the sulfate ion

content. Small corrections were made to account for unmeasured sulfate (HSO_4^- and $AlSO_4^+$) in the ion chromatography analysis and residual filtrate in the fiber pad before acidification (Appendix XIII).

Aluminum Sulfate Desorption Experiments

Desorption experiments were conducted to understand how the polymer adsorbed. Since the polymer was added after 10 minutes of aluminum adsorption, there was a possibility that some polymer could be adsorbed onto previously adsorbed aluminum. By desorbing the aluminum, this polymer should also desorb. However, unless precautions were taken, the desorbed polymer could then adsorb onto the freshly exposed cellulose surface.

The following procedure was used. First, aluminum sulfate was adsorbed for 10 minutes at a chosen pH, then the polymer was adsorbed for 1 minute. Before aluminum desorption, 0.124 g of a 50% cationic surfactant solution, trimethyldodecylammonium chloride (TDA), was added to prevent the readsorption of the polymer onto freshly exposed cellulose. Sikora[55] found that TDA diffused more quickly to the negative adsorption sites, thus preventing further polymer adsorption. The aluminum was then desorbed by addition of 0.1N HCl to pH 3.5. Samples were collected according to the normal adsorption run procedure and analyzed for unadsorbed polymer. Next, the above procedure was repeated without acidification to determine the effect of TDA on polymer adsorption and to serve as a controlled experiment. The difference between polymer adsorption in the desorption experiment and the controlled experiment represented the amount of desorbed polymer, i.e., the polymer which adsorbed onto previously adsorbed aluminum under the controlled conditions. The desorption and controlled experimental procedures were repeated at other pH's during the aluminum and polymer adsorption step.

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE CATIONIC POLYELECTROLYTE

The characteristic properties of the cationic polyelectrolyte are presented in Table 4.

Table 4. Characteristic properties of the cationic polyelectrolyte.

Charge	3.0 ± 0.1 mole percent net cationic charge[a] 0.25 mole percent anionic charge ± 20%
Molecular weight	880,000 ± 20,000 g/mole[a]
Radioactivity (^{14}C and ^{3}H window)	1730 ± 50 cpm/μg polymer[a]

[a]95% confidence limits.

The net charge is representative of a low-charge polyelectrolyte. The molecular weight corresponds to a high molecular weight polyelectrolyte. The anionic charge represents a slight degree of hydrolysis, which is undesired, but often present in commercial polyelectrolytes.[47,56,57] The degree of hydrolysis is very small compared to the net charge. The radioactivity is sufficient for accurate counting of the adsorption run samples.

ALUMINUM ADSORPTION

Initial Considerations

Aluminum salt, aluminum concentration, and pH were initially selected as the principal variables in studying the adsorption of aluminum. The aluminum salts were aluminum chloride and aluminum sulfate. The aluminum concentration was set at 2.5×10^{-4}, 5.0×10^{-4}, and 10.0×10^{-4} M. The pH was varied from 4.1 to 5.5. The time for aluminum adsorption was held constant at 10 minutes.

The amount of aluminum adsorbed is expressed on a weight/weight basis as mg aluminum/g cellulose because it is impossible to know with certainty what the adsorbing aluminum species is. In terms of relative adsorption, 100% adsorption of the aluminum by the fibers or complete removal of the aluminum from solution is at 2.27 mg aluminum/g cellulose at 2.5×10^{-4}M, 4.54 mg aluminum/g cellulose at 5.0×10^{-4}M, and 9.08 mg aluminum/g cellulose at 10.0×10^{-4}M.

Effect of pH

The effect of pH on aluminum adsorption for $AlCl_3$ and $Al_2(SO_4)_3$ is presented in Fig. 10. For direct comparison, the pHp's for $AlCl_3$ and $Al_2(SO_4)_3$, as determined by Hayden and Rubin, are included. The adsorption of $AlCl_3$ is similar to that observed by Arnson. However, the adsorption of $Al_2(SO_4)_3$ differs from Arnson's study. With $Al_2(SO_4)_3$, the increase in adsorption occurs after the pHp and, therefore, appears related only to the precipitate of the aluminum. This relationship has been confirmed by the use of two pH meters, each with their own electrodes, for a few aluminum adsorption curves.

At this point, the interpretation of the aluminum adsorption results is impossible due to (1) inconsistencies between this study and Arnson's study, (2) differences between $AlCl_3$ and $Al_2(SO_4)_3$ adsorption in relation to the pHp's, and (3) the absence of pHp values, as determined in the presence of cellulosic fibers.

Determination of pHp's

Due to inconsistencies in the aluminum adsorption results, the pHp's for $AlCl_3$ and $Al_2(SO_4)_3$ in the presence and absence of cellulosic fibers were determined. Light scattering was used to detect the formation of the aluminum precipitates. The pHp's in the absence of fibers were determined by light scattering measurements of the aluminum salts in KCl-free distilled water at various

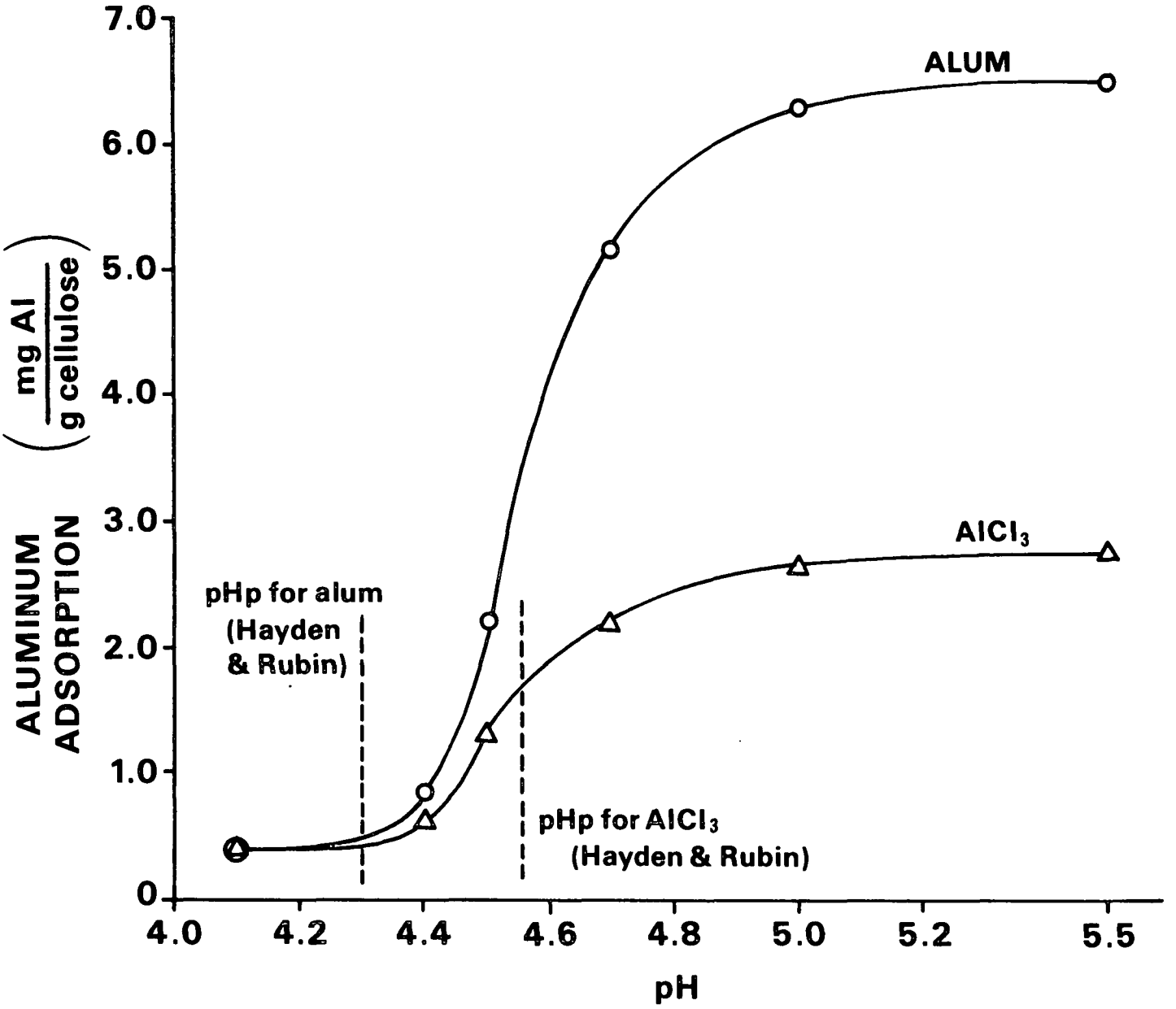

Figure 10. Aluminum adsorption as a function of pH for $AlCl_3$ and $Al_2(SO_4)_3$ at 10.0×10^{-4} M Al. Dashed vertical lines denote the pH of precipitation formation (pHp) for each aluminum salt.

pH's. The pHp's in the presence of fibers were determined by light scattering measurements on the filtrate samples of aluminum adsorption experiments (0.01M KCl) at various pH's. These latter samples contained fines which also contributed to the scattering of light. However, by acidifying the samples, the fines contribution could be measured and then subtracted from the overall measurements.

The light scattering measurements as a function of pH for $Al_2(SO_4)_3$ at 10.0×10^{-4}M aluminum are presented in Fig. 11. For a direct comparison the aluminum adsorption curve at the same concentration is presented in the bottom half of the figure. There is good agreement among the experimentally determined pHp's in the presence and absence of fibers and the pHp value cited by Hayden and Rubin. This confirms that the higher aluminum adsorption occurs after the pHp and is due only to the presence of the aluminum precipitate. This is in contrast to Arnson's results in which the break in aluminum adsorption occurs before the pHp.

The light scattering measurements as a function of pH for $AlCl_3$ at 5.0×10^{-4}M and 10.0×10^{-4}M are presented in Fig. 12 and 13, respectively. As with $Al_2(SO_4)_3$ the experimentally determined pHp's in the absence of fibers agree well with the values cited by Hayden and Rubin. However, the pHp's determined in the presence of fibers occur at a lower pH. The presence of fibers apparently shifts the pHp's to lower pH's. The lower pHp's should be the correct pHp's for the aluminum adsorption experiments. In both figures, the break in $AlCl_3$ adsorption is in alignment with the correct pHp. Therefore, $AlCl_3$ adsorption is similar to $Al_2(SO_4)_3$ adsorption; that is, only the aluminum precipitate is responsible for the increased levels of aluminum adsorption.

Additional light scattering tests were conducted to determine the cause of the lower pHp's in the $AlCl_3$ adsorption experiments. Besides distilled

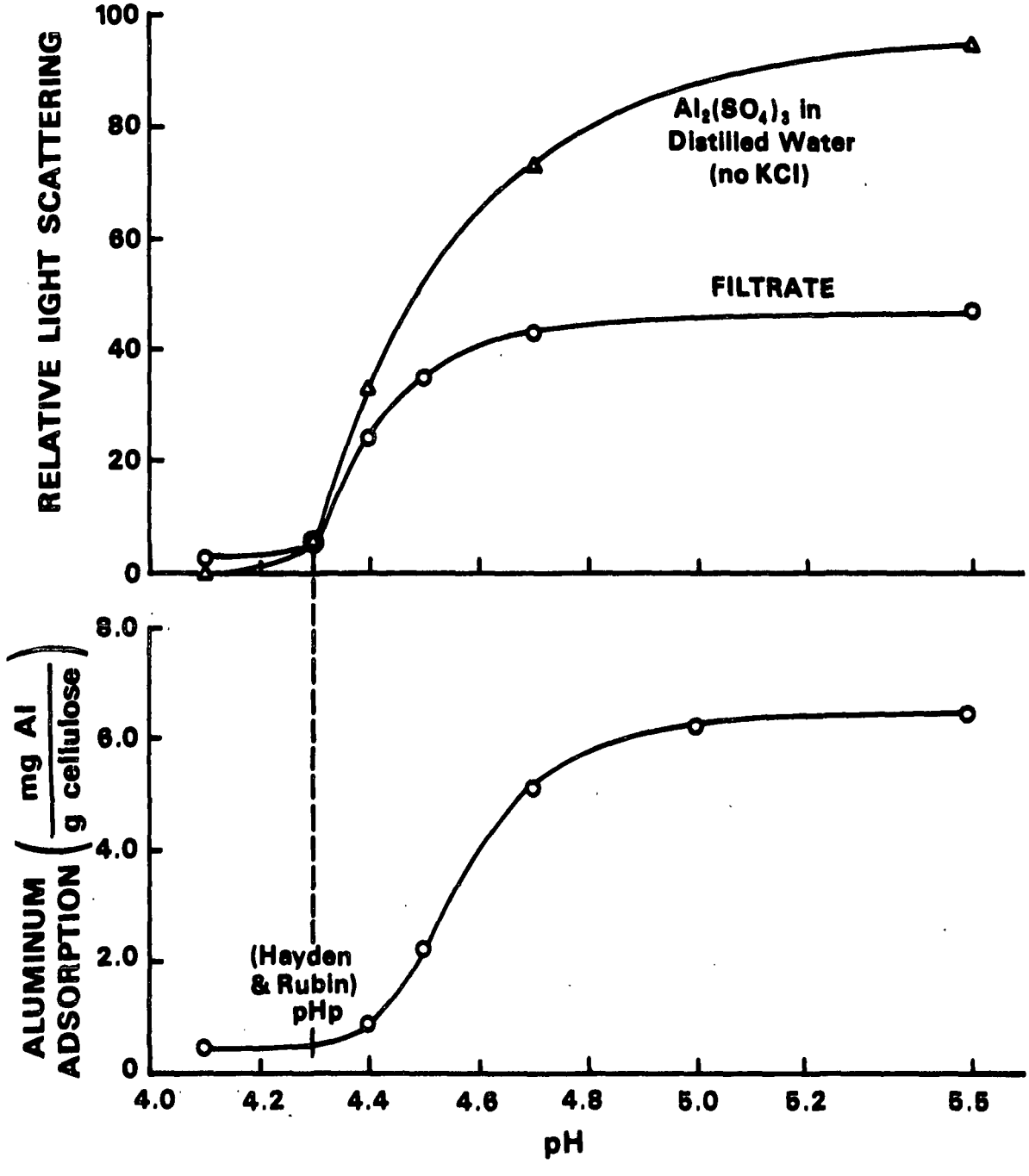

Figure 11. Top: Light scattering as a function of pH for $Al_2(SO_4)_3$ (effect of stock on pHp) (10.0×10^{-4}M Al).
Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (10.0×10^{-4}M Al).

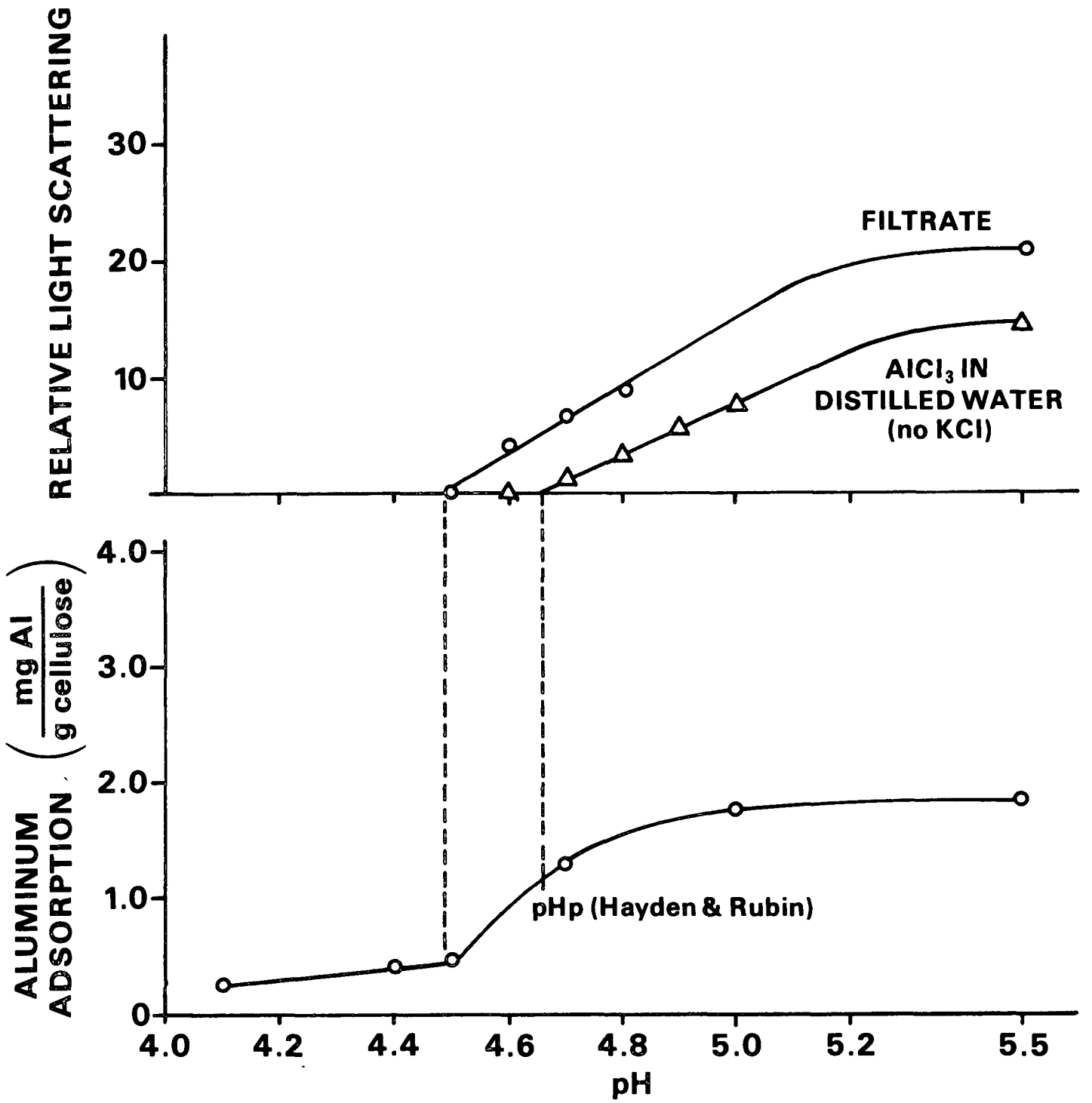

Figure 12. Top: Light scattering as a function of pH for $AlCl_3$ (effect of stock on pHp) (5.0×10^{-4}M Al).
Bottom: Aluminum adsorption as a function of pH for $AlCl_3$ (5.0×10^{-4}M Al).

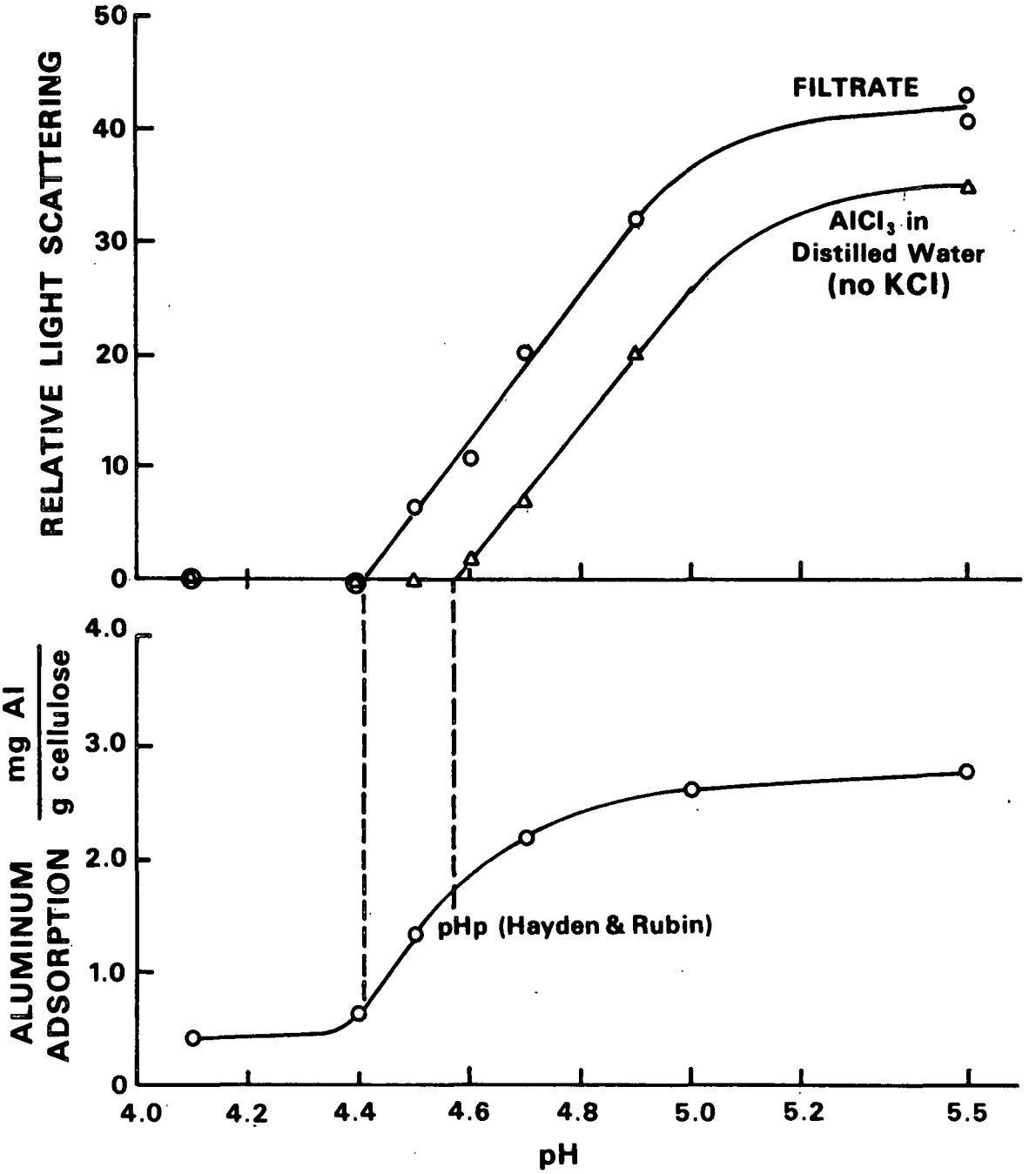

Figure 13. Top: Light scattering as a function of pH for $AlCl_3$ (effect of stock on pHp) (10.0×10^{-4}M Al).
Bottom: Aluminum adsorption as a function of pH for $AlCl_3$ (10.0×10^{-4}M Al).

water and $AlCl_3$ the adsorption experiments contained 0.01N KCl, fibers, and fines. Light scattering tests conducted in 0.01N KCl give a pHp identical to that of $AlCl_3$ in distilled water (Fig. 14). Therefore, fibers and/or fines were responsible for the lower pHp's. Fines should have the same effect as fibers, except for the fines that passed through the 10 μm pore size filter and into the light scattering samples. Since the light scattering samples contained some fines, there was a possibility that pH affected the flocculation of fines in the presence of $AlCl_3$ which in turn may have affected the light scattering and produced false pHp's at lower pH's. To determine the effect of fines, $AlCl_3$ was added to a solution of fines. The fines solution was obtained from the decantation of a 0.3% consistency stock solution of cotton linters after the fibers had settled. The level of fines corresponded to the amount present in the filtrate samples of the standard aluminum adsorption runs. The light scattering tests conducted in the presence of fines, but in the absence of fibers, give a pHp identical to that of $AlCl_3$ in distilled water (Fig. 15). Therefore, the lower pHp's were not due to the flocculation behavior of fines at various pH's. In addition light scattering is unaffected by fines retention since all tests with $AlCl_3$ give similar fines level as a function of pH. By the process of elimination, only the fibers can be responsible for the lowering of the pHp's in the $AlCl_3$ adsorption experiments.

To speculate about the effect of fibers on the pHp's one must understand how the precipitate behavior of $AlCl_3$ differs from that of $Al_2(SO_4)_3$. According to Hayden and Rubin, $AlCl_3$ solutions near the pHp are initially highly oversaturated. With time they experienced a shift of the pHp's to lower pH's as the solutions destabilized. However, their $Al_2(SO_4)_3$ solutions did not appear as highly supersaturated near the pHp. Time had very little effect on the pHp's of $Al_2(SO_4)_3$ solutions. Perhaps, in my study, the negative fiber surface

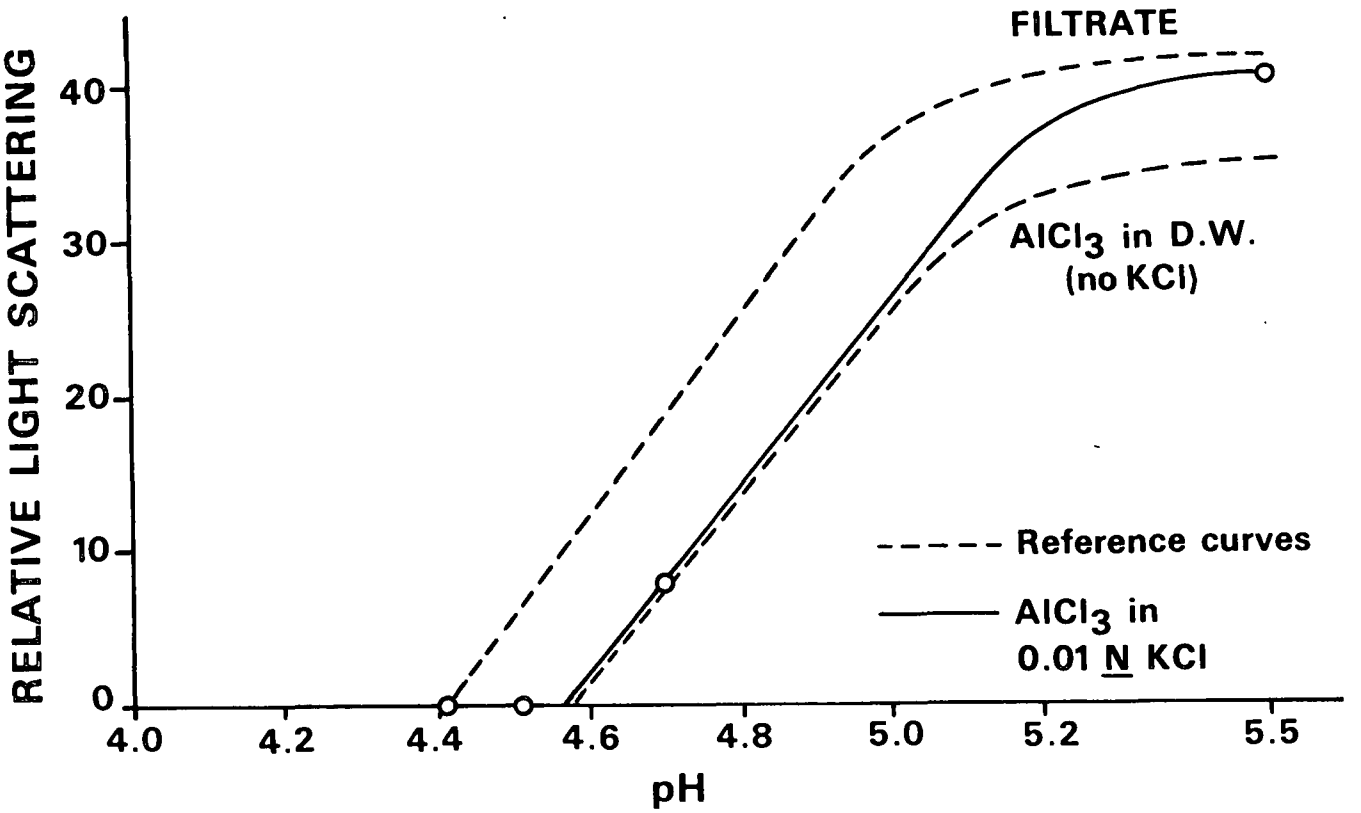

Figure 14. Light scattering as a function of pH for $AlCl_3$ (effect of 0.01N KCL on pHp) (10.0×10^{-4}M Al).

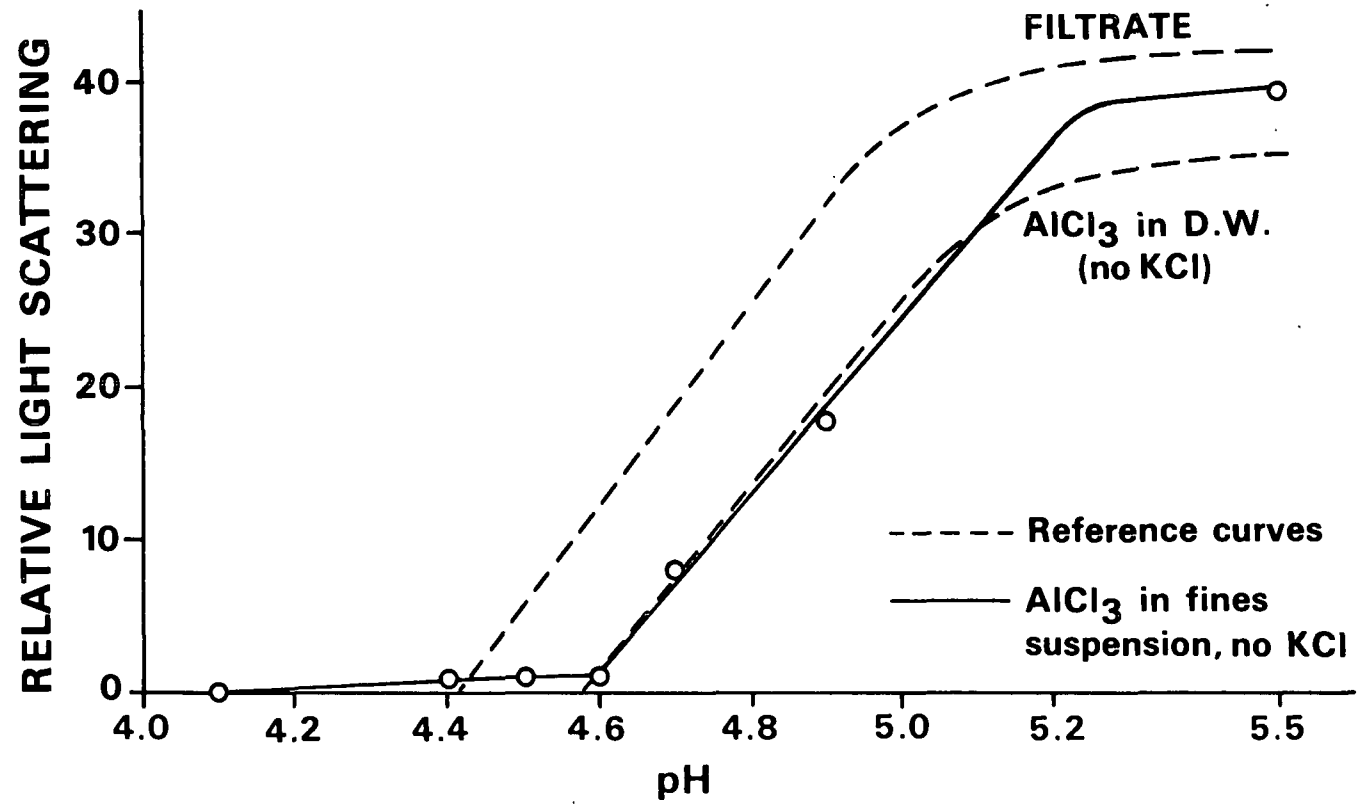

Figure 15. Light scattering as a function of pH for $AlCl_3$ (effect of fines on pHp) (10.0×10^{-4}M Al).

destabilized the supersaturated $AlCl_3$ solution near the pHp by increasing the aluminum concentration near the fiber surface through electrostatic attraction. This may explain why the pHp's of $AlCl_3$ solutions are lower in the presence of the cotton linters.

Effect of pH and Aluminum Concentration

Aluminum adsorption as a function of pH and aluminum concentration is presented in Fig. 16 and 17 for $AlCl_3$ and $Al_2(SO_4)_3$, respectively. For comparison, the pHp's are included. For $AlCl_3$ the pHp values were experimentally determined at the highest two concentrations. For $Al_2(SO_4)_3$ the pHp values were taken from Hayden and Rubin's study. As a function of pH, the shape of the adsorption curves are similar. $Al_2(SO_4)_3$, however, exhibits a higher adsorption above the pHp. With both aluminum salts, aluminum adsorption is dependent upon aluminum concentration throughout the pH range.

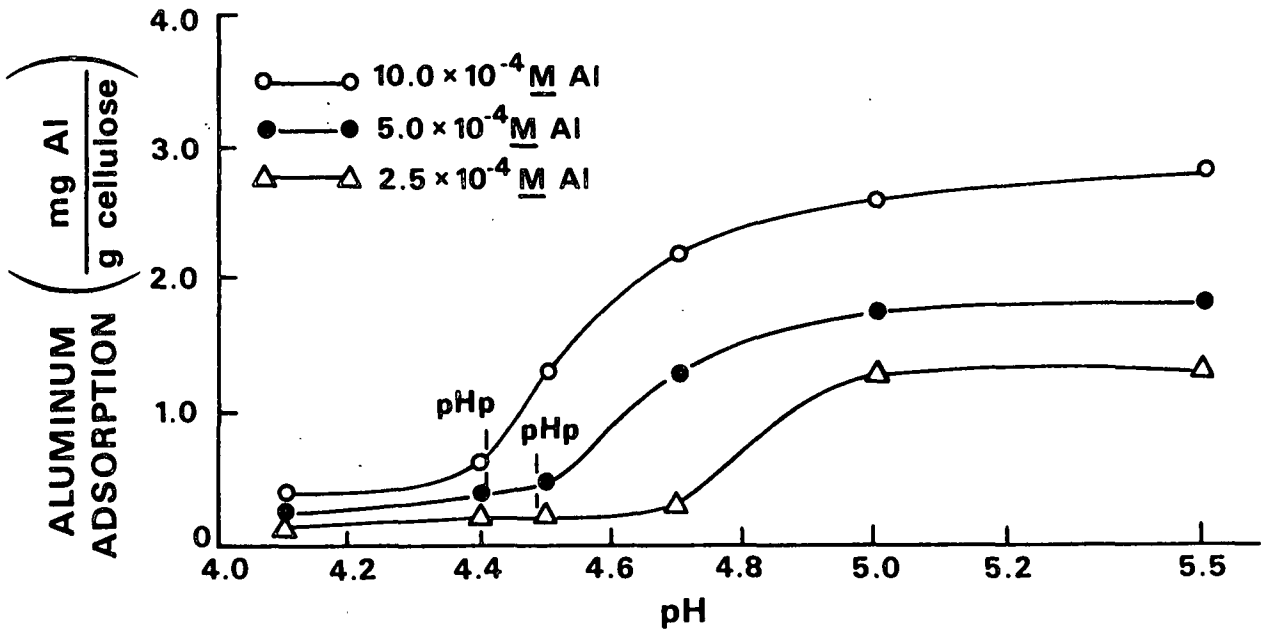

Figure 16. Aluminum adsorption as a function of pH and aluminum concentration for $AlCl_3$.

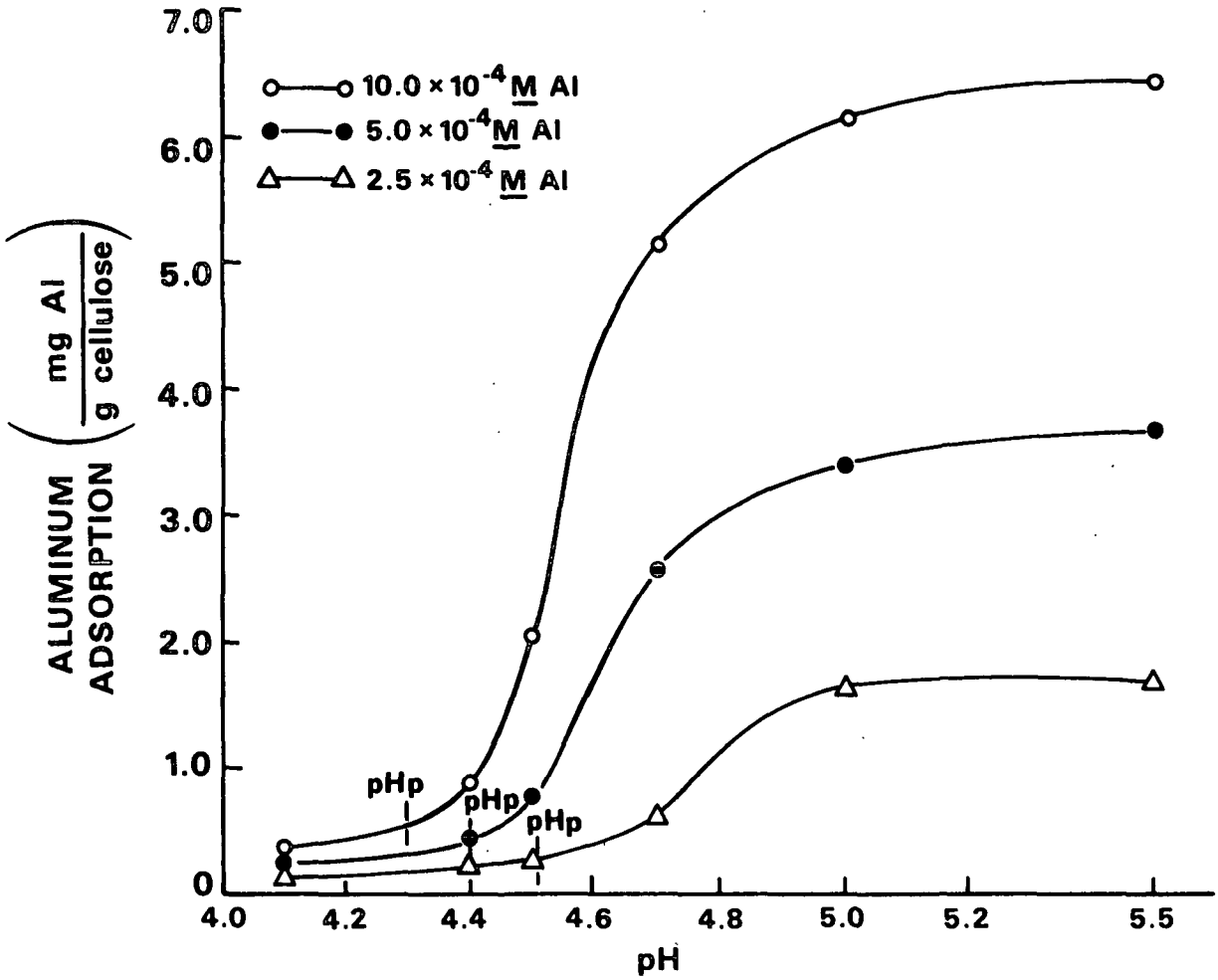

Figure 17. Aluminum adsorption as a function of pH and aluminum concentration for $Al_2(SO_4)_3$.

The effect of aluminum concentration on aluminum adsorption can also be presented as in Fig. 18. Again, it is apparent that (1) aluminum adsorption increases with aluminum concentration and (2) aluminum sulfate adsorbs to a much stronger degree than $AlCl_3$ at high pH. At high pH both aluminum salts show similar trends: after the initial adsorption, the adsorption appears fairly linear with respect to aluminum concentration.

Some of these observations were reported by Arnson, such as (1) the similar shapes of the adsorption curves as a function of pH, (2) the higher adsorption of $Al_2(SO_4)_3$ above the pHp, (3) the concentration dependent effect above the break in aluminum adsorption, and (4) a relationship between the pHp and the break in aluminum adsorption. However, he did not observe the concentration dependent effect below the break in aluminum adsorption nor did he observe an alignment of the pHp and the break in aluminum adsorption.

The contradiction between studies below the break in aluminum adsorption may be explained by the development of a more sensitive aluminum analysis for the present study. A sensitive analysis is necessary at the low pH since very little aluminum adsorbs as compared with the high concentration of unadsorbed aluminum which is analyzed.

The contradiction between studies on the significance of the break in aluminum adsorption is related to the effect of fibers on the pHp in the $AlCl_3$ case (Fig. 12 and 13) and the disagreement in the pH at which the break in aluminum adsorption occurs in the $Al_2(SO_4)_3$ case (compare Fig. 6, p. 20 to Fig. 17). Values for pHp, in the presence of fibers, were never determined in Arnson's study. The disagreement in the pH at which the break occurs has yet to be resolved. However, some of my results have been verified by using two sets of electrodes with two pH meters.

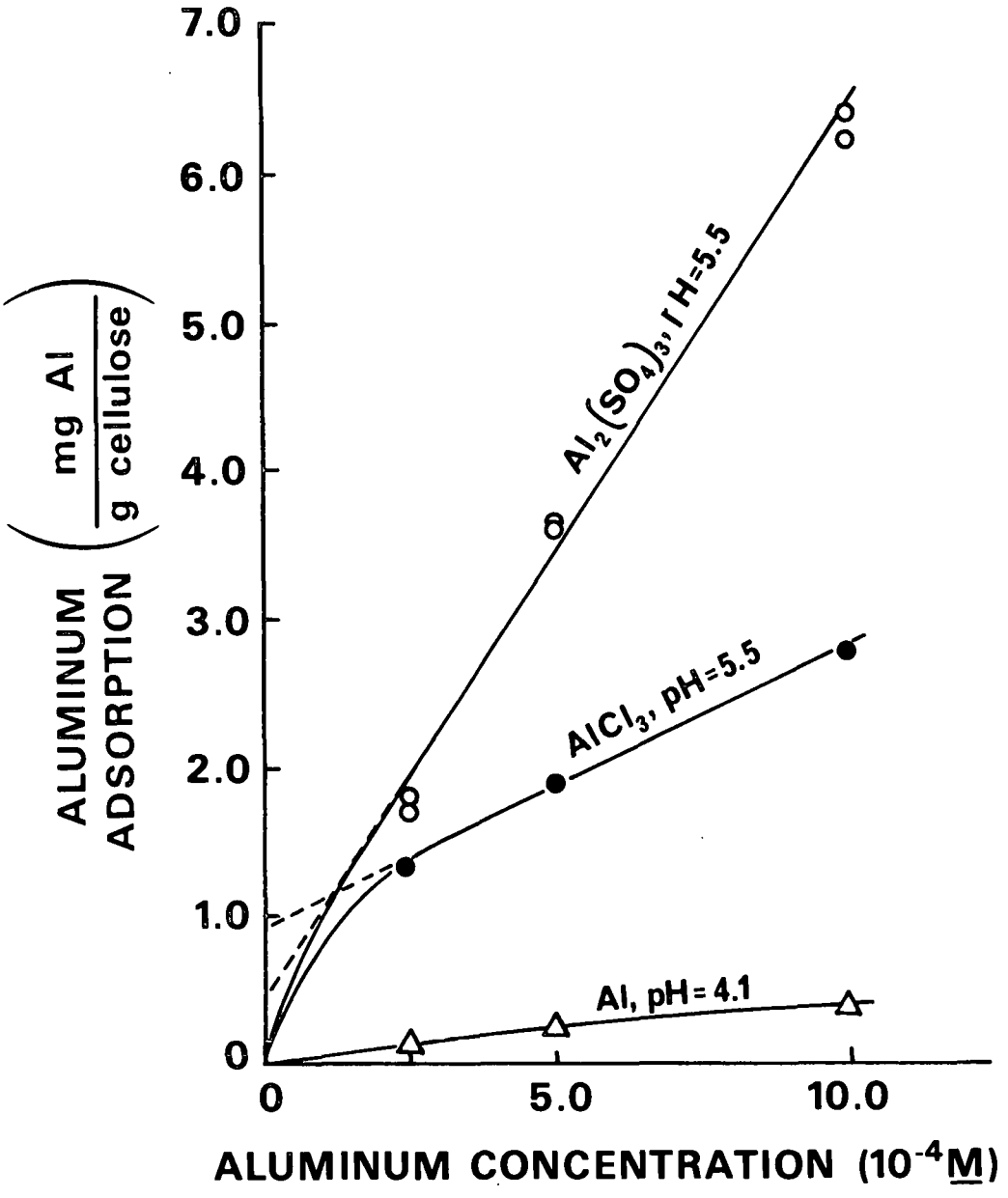

Figure 18. Aluminum adsorption as a function of aluminum concentration and pH.

Investigation of Mechanisms

Additional experiments have been conducted to determine the mechanisms by which aluminum adsorbs.

Effect of Aluminum Adsorption on Fiber Charge

The effect of aluminum salts on fiber charge is presented in Fig. 19. Two aluminum concentrations were examined. Zeta potential of the fines was used as a measure of fiber charge. The zeta potential in the absence of aluminum was approximately -12 mV. At all pH's the zeta potential increases in the presence of aluminum salts. However, the zeta potential is fairly concentration independent in this range of concentration. Below the pHp the zeta potential remains negative. In this region there are no significant differences between the zeta potentials of the two aluminum salts at either concentration. At the pHp the zeta potential is zero. Above the pHp the fiber charge is reversed. In this region the zeta potential still appears to be independent of aluminum concentration and adsorption. The only variation in zeta potential above the pHp is between the two aluminum salts. Aluminum chloride, which adsorbs to a lesser degree, imparts a higher cationic charge to the fiber.

The effect of aluminum adsorption on zeta potential can also be represented as in Fig. 20. Again one can see that (1) zeta potential increases in the presence of aluminum salts, (2) the zeta potential is fairly concentration independent from 5.0×10^{-4}M to 10.0×10^{-4}M Al, and (3) the precipitate in the case of $AlCl_3$ has the greatest effect on zeta potential, even though it adsorbs less than $Al_2(SO_4)_3$. However, in addition one can see that the concentration independent behavior on zeta potential in the presence of aluminum precipitates occurs in the linear region of the adsorption curves. Apparently, the charge

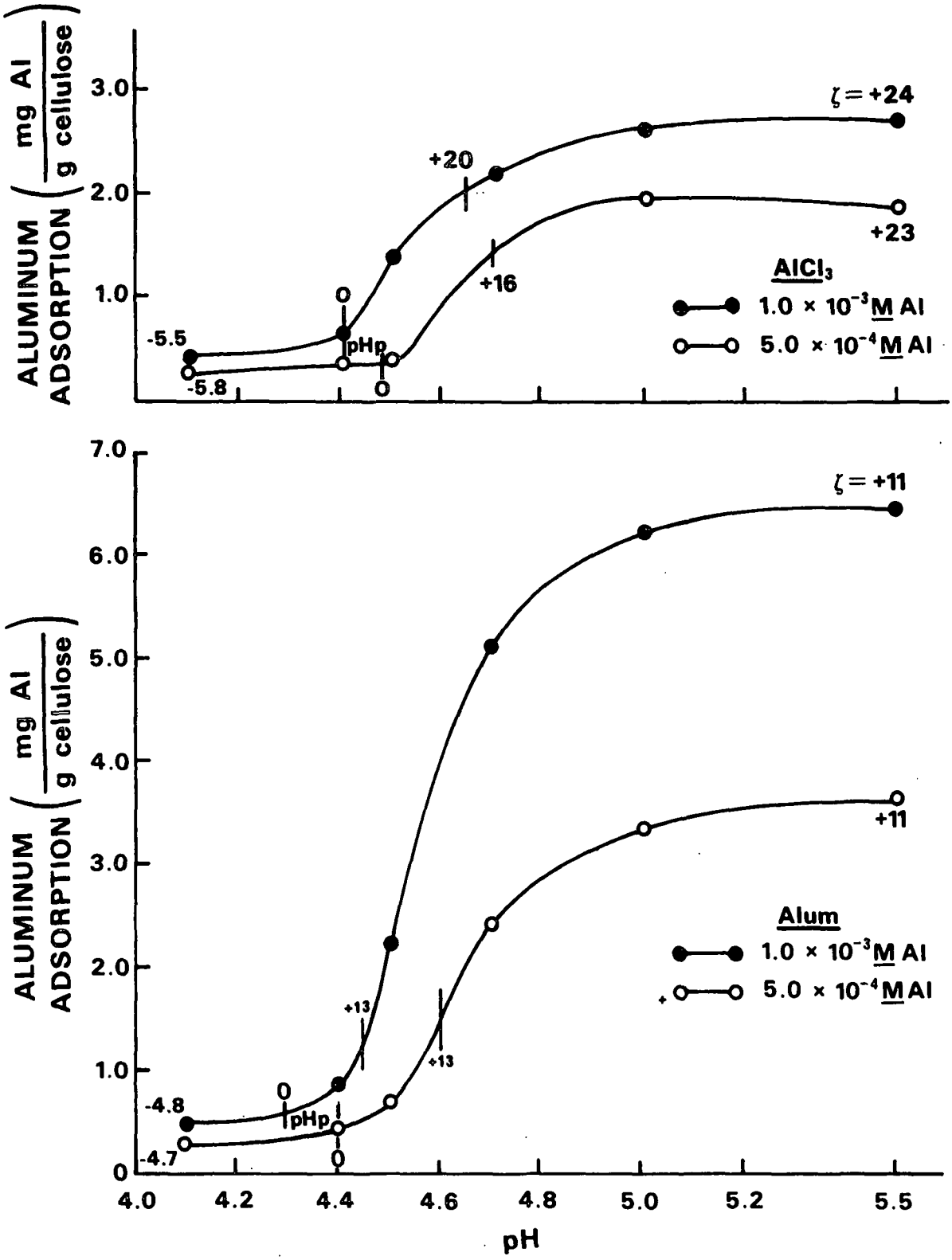

Figure 19. Top: Zeta potential values as related to pH and adsorption for $AlCl_3$.
Bottom: Zeta potential values as related to pH and aluminum adsorption for $Al_2(SO_4)_3$.

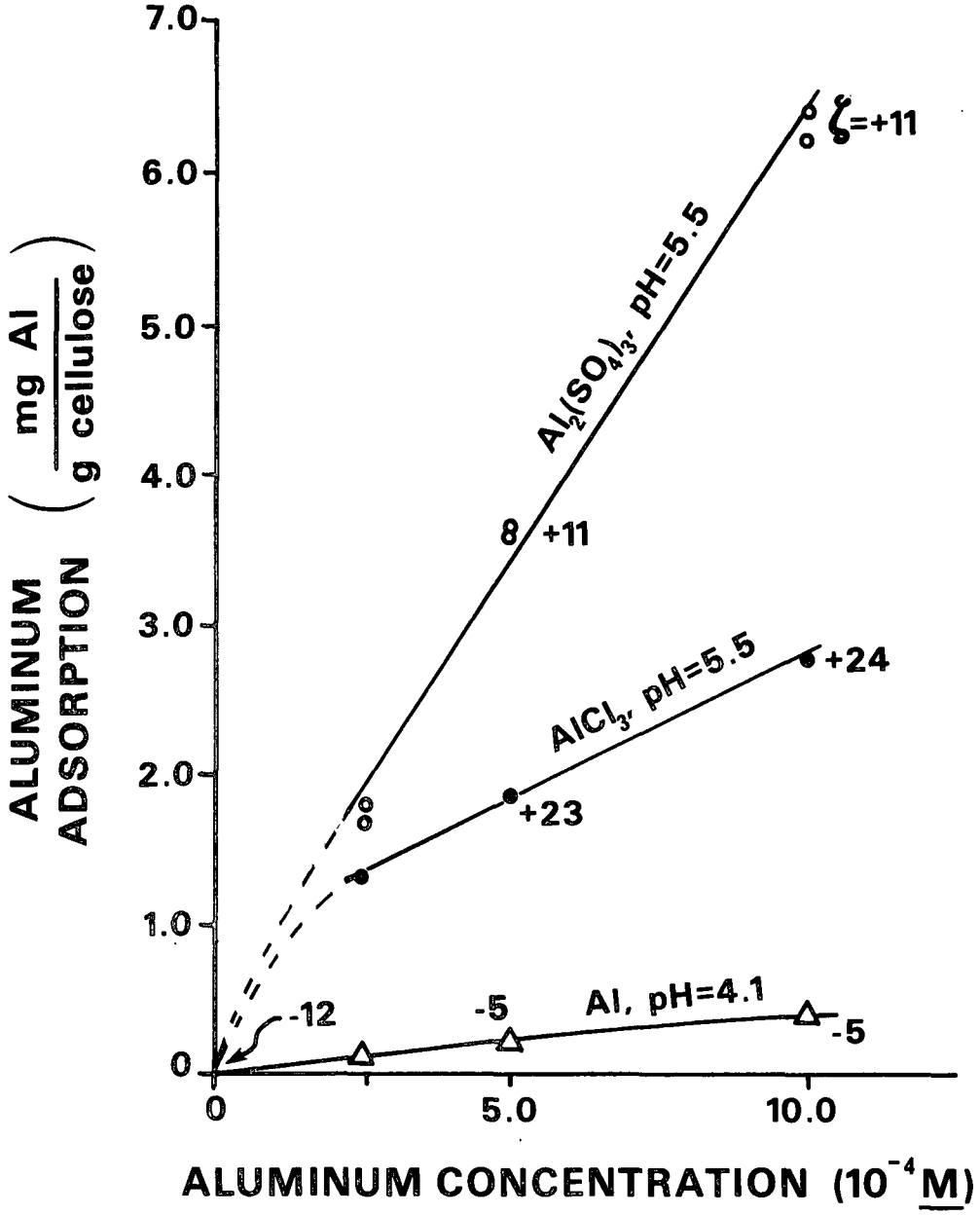

Figure 20. Zeta potential values as related to pH, aluminum concentration, and aluminum adsorption.

reversal of the fibers in the presence of the aluminum precipitates occurs at the lowest levels of addition where the adsorption curves are nonlinear.

Aluminum Sulfate Precipitate Analysis

An analysis of the aluminum sulfate precipitate was conducted to further understand the differences between $AlCl_3$ and $Al_2(SO_4)_3$ solutions above their pHp's. The precipitate was formed from a 4.0×10^{-4}M Al solution at pH 5.5 in the presence of cotton linters. The precipitate was isolated by adsorption onto cotton linters and recovered by desorption into acidified water. After desorption the acidified water was analyzed for aluminum and sulfate. The results indicated approximately 1 mole sulfate per 4.2 moles of aluminum.

Interpretation of the Aluminum Adsorption Results

Below the pHp

Below the pHp where only soluble aluminum species exist, the adsorption of aluminum is extremely low. This low level of adsorption would be expected from the soluble species if they adsorbed by a simple ion exchange mechanism. Since an ion exchange mechanism can allow only up to one adsorbed ion per carboxyl group, multilayer adsorption should not occur. If the adsorption of trivalent aluminum ions is assumed, then the adsorption would be less than or equal to 1.1 mg/g cellulose. The actual adsorption levels (0.1-0.5 mg/g cellulose) are within this range.

The ion exchange mechanisms would permit the concentration dependent behavior of the aluminum adsorption as observed in Fig. 16 and 17. The ion exchange mechanism can be expressed by the following equilibrium:

$$y(RCOO^-) + \left(\begin{matrix}\text{Soluble} \\ \text{Al species}\end{matrix}\right)^x \rightleftharpoons (RCOO^-)_y \left(\begin{matrix}\text{Soluble} \\ \text{Al species}\end{matrix}\right)^{x-y}$$

As the aluminum concentration is increased, so is the aluminum adsorption. The ion exchange mechanism would also permit greater aluminum adsorption as the carboxyl content of the pulp is raised. This dependency on the carboxyl content has been observed in several studies.[2,58-61]

The trivalent aluminum ion would be the most probable soluble species to adsorb due to its superior charge density and concentration over the other species. This adsorption of Al^{3+} is supported by the aluminum adsorption results at the lowest pH. In this region Al^{3+}, $AlSO_4^+$, and $AlOH^{2+}$ are the only aluminum species according to Hayden and Rubin.[1] The effect of $AlSO_4^+$ must be insignificant due to the similar adsorption results of both aluminum salts. This leaves Al^{3+} and $AlOH^{2+}$. The Al^{3+}, however, has a concentration 20-25 times greater than the $AlOH^{2+}$ at all $AlCl_3$ concentrations considered in this investigation. In terms of the simple adsorption competition mechanism, Al^{3+} would be expected to be the primary aluminum species adsorbed in this region because of its superior concentration and charge.

At higher pH's, but still below the pHp, the aluminum adsorption does not change significantly. In this region polynuclear species may be formed in the presence of Al^{3+} and $AlOH^{2+}$. However, if polynuclear species form, they do not appear to have any differing effects on aluminum adsorption or polymer adsorption (discussed later). If these species are adsorbed preferentially over the Al^{3+} ion, then a much higher aluminum adsorption should be expected due to the high number of aluminum atoms per ion. However, significantly higher aluminum adsorption was not observed. The polynuclear species probably possess a higher charge; however, Al^{3+} has a much smaller ionic radius. Therefore, in terms of the simple adsorption competition mechanism, Al^{3+} would be expected to be preferentially adsorbed because of its superior charge density.

Later results (p. 100) comparing the effects of aluminum and lanthanum (a nonhydrolyzing trivalent cation up to pH 8) on the adsorption of polymer also support the preferential adsorption of the trivalent aluminum ion.

Above the pHp

Above the pHp the precipitated aluminum species are the predominant species. The increased adsorption of aluminum in this region would be expected to be attributed to the formation of the precipitate. The adsorption at pH > 5.0 is fairly well understood and has been discussed by other workers.[62-64] In general it is believed that the colloidal precipitate comes out of solution and accumulates at the liquid-solid interface on the surface of the fibers. At the surface it will become enmeshed in the fibrillar structure of the fiber and be bound through short range molecular forces.

In this pH range (5.0-5.5) the precipitate has a strong positive charge and may be considered a charged colloidal particle.[62,65,66] This is supported by this study (Fig. 20). Part of the forces of attachment would, therefore, be expected to be electrostatic in nature. This is supported by Arnson's results in which he varied the carboxyl content while adsorbing $AlCl_3$ from a 2.5×10^{-4}M solution at pH 5.5. The higher aluminum adsorption at the higher carboxyl content was interpreted to be due to electrostatic attraction between the aluminum precipitate and the fiber surface.

My results would appear to indicate that electrostatic attraction between the aluminum precipitate and the fiber surface is only present at low levels of aluminum adsorption. Up to an adsorption of approximately 1.5 mg aluminum/g cellulose strong adsorption occurs (Fig. 20). In this region the zeta potential went from negative (-12 mV) to positive (+11 or +24 mV).

Apparently the cationic precipitate strongly interacts with the negative fiber surface, thus supporting the view that electrostatic attraction improves adsorption at low levels of aluminum. Above this level ($\geq$ 2.5 x 10^{-4}M Al addition), the adsorption is a linear function of aluminum addition and the fiber charge appears constant. Apparently the carboxyl groups are essentially covered with the cationic precipitate and further adsorption has no effect on the characteristics of the fiber surface. Therefore, the carboxyl groups will have no further effect and the electrostatic interaction will remain constant with further adsorption. So an increase in aluminum addition will cause a correspondingly linear increase in aluminum adsorption.

Aluminum sulfate, which forms a less cationic precipitate as compared with $AlCl_3$, would be expected to experience less electrostatic attraction to the fiber. As seen in Fig. 20, the $Al_2(SO_4)_3$ adsorption curve is more linear at the lower addition, thus supporting this statement. However, $Al_2(SO_4)_3$ still is adsorbed to a greater extent than $AlCl_3$. Due to the lower charge of the $Al_2(SO_4)_3$ precipitate there is probably less electrostatic repulsion between the unadsorbed and the adsorbed aluminum precipitate.

Aluminum sulfate forms a less cationic precipitate due to sulfate ions. According to the precipitate analysis it contains approximately 1 mole sulfate per 4.2 moles of aluminum. The exact chemical structure of the $Al_2(SO_4)_3$ precipitate has never been determined. However, its lesser cationic charge is probably due to either the incorporation of the sulfate ion into the precipitate or the screening of cationic charges by the sulfate ion acting as a counterion.

POLYMER ADSORPTION

Initial Considerations

Except for the adsorption isotherm results, polymer concentration, polymer adsorption time, and pH were selected as the principal variables in studying the adsorption of polymer in the absence of aluminum salts. The polymer concentration was set at 3.0 ppm (0.10% polymer addition) and 1.5 ppm (0.05% polymer addition). The polymer adsorption time was set at either 15 seconds or 10 minutes. The pH was varied from 4.1 to 5.5.

The amount of polymer adsorbed is expressed on a weight/weight basis as mg polymer/g cellulose. In terms of relative adsorption, 100% adsorption of the polymer by the fibers is at 1.0 mg polymer/g cellulose at 3.0 ppm addition and 0.5 mg polymer/g cellulose at 1.5 ppm addition. In addition, except for Fig. 21, 22, 38, and 42-44, in which polymer addition is varied, polymer adsorption can be easily represented as relative adsorption (%), since each marked interval on the y-axis corresponds to a change of 20% adsorption.

Equilibrium Adsorption Isotherm

An equilibrium adsorption isotherm was constructed to determine (1) whether the synthesized polymer adsorbs strongly (i.e., close to 100%) and (2) how much polymer the cellulose surface can adsorb. At low polymer additions ($<$ 18 ppm), the adsorption time was varied from 10 min to 120 min with no significant effect on adsorption. At high polymer additions ($>$ 60 ppm) the adsorption time was set at 90 minutes. Figure 21 presents adsorption as a function of polymer addition. A 100% adsorption reference line is included. Between 1.5 and 3.0 ppm the adsorption is approximately 87%.

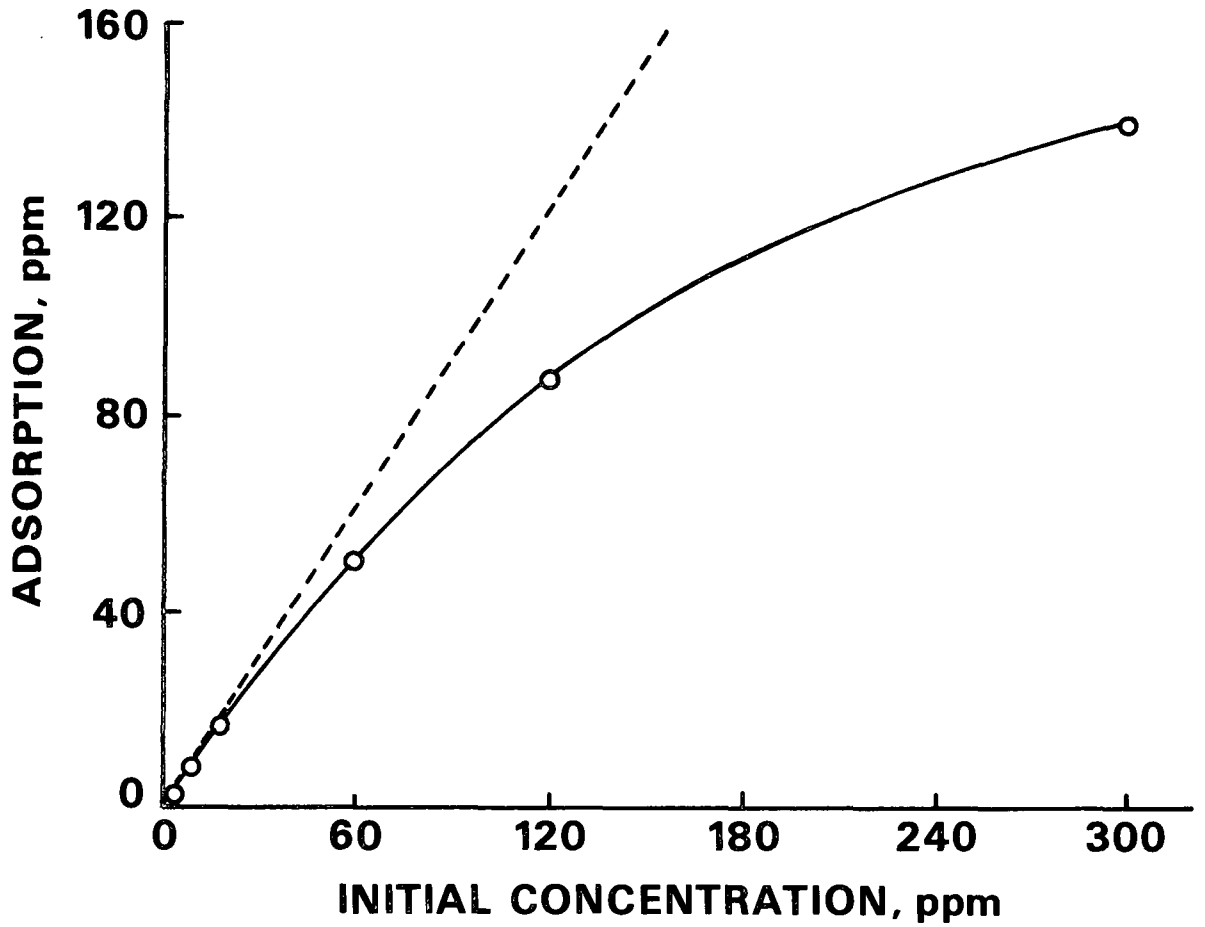

Figure 21. Equilibrium adsorption isotherm in the absence of KCl. A dashed line representing 100% adsorption is included for reference (cotton linters = 3.0 g/L) (adsorption time = 90 min).

The Langmuir equation[67] was employed to determine the maximum adsorption level.

$$C_* = KC_MC_e/(1 + KC_e)$$

where C_* = specific adsorption at the equilibrium concentration, C_e, ppm

K = Langmuir constant

C_M = maximum amount adsorbed, ppm

The Langmuir equation can be rearranged in the following manner:

$$\frac{C_e}{C_*} = \frac{1}{KC_M} + \frac{C_e}{C_M}$$

A plot of C_e/C_* vs. C_e has a slope of $1/C_M$ and an intercept of $1/KC_M$. The values of C_M and K are obtained by regression analysis. The relationship is

approximately linear (Fig. 22), which is characteristic of Langmuir-type behavior. At a 95% confidence level the maximum amount adsorbed was calculated to be 152 ± 15 ppm or 51 ± 5 mg polymer/g cellulose.

Effect of pH, Polymer Concentration, and Adsorption Time

The effect of pH at 3.0 ppm and 1.5 ppm polymer additions is presented in Fig. 23. Polymer adsorption in the top half of Fig. 23 is expressed in mg polymer/g cellulose, while polymer adsorption in the bottom half of Fig. 23 is expressed as relative adsorption (%). As seen in Fig. 23 a lower relative adsorption (≈ 60-80%) occurs in the presence of 0.01N KCl as compared to the equilibrium adsorption isotherm results (≈ 87%). This is probably due to either nonequilibrium conditions (15 seconds adsorption time) and/or competition with potassium for adsorption. There is also a slight reduction in adsorption when the pH is lowered. This is probably due to the change in ionization of the cellulose carboxyl groups. These effects were not significant enough to warrant an in-depth investigation.

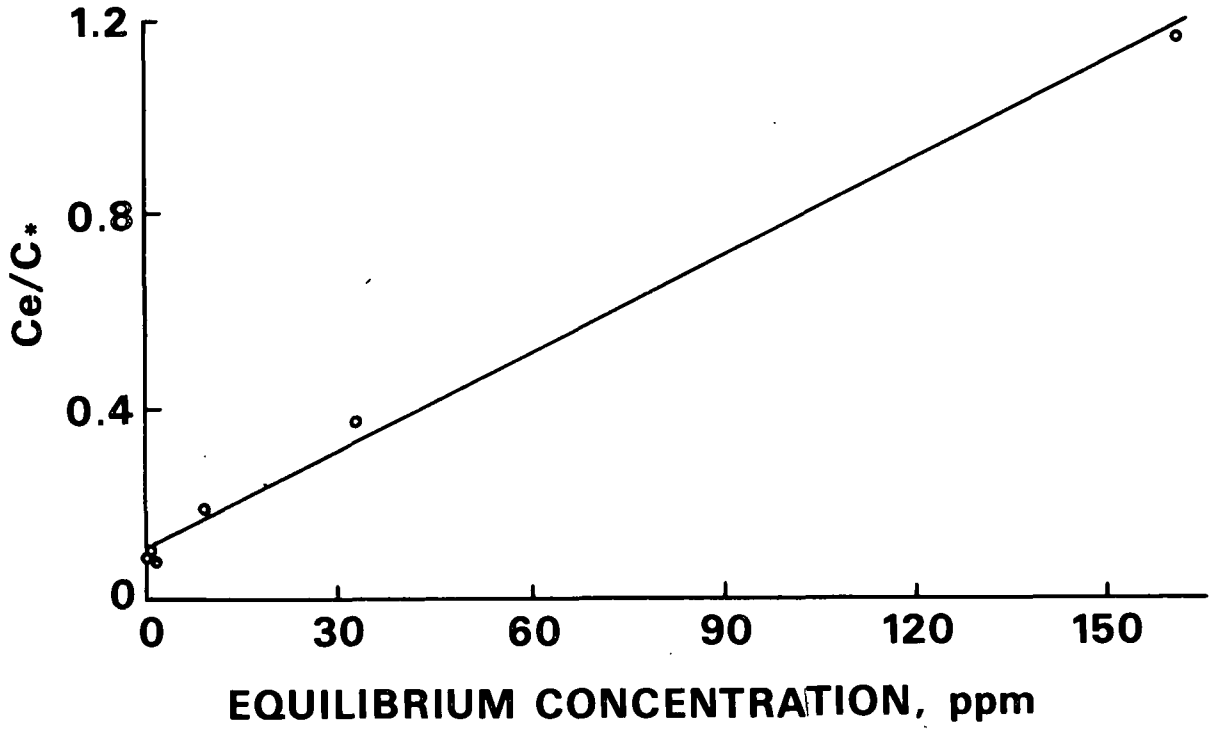

Figure 22. Equilibrium adsorption isotherm in the absence of KCl (cotton linters = 3.0 g/L) (adsorption time = 90 min).

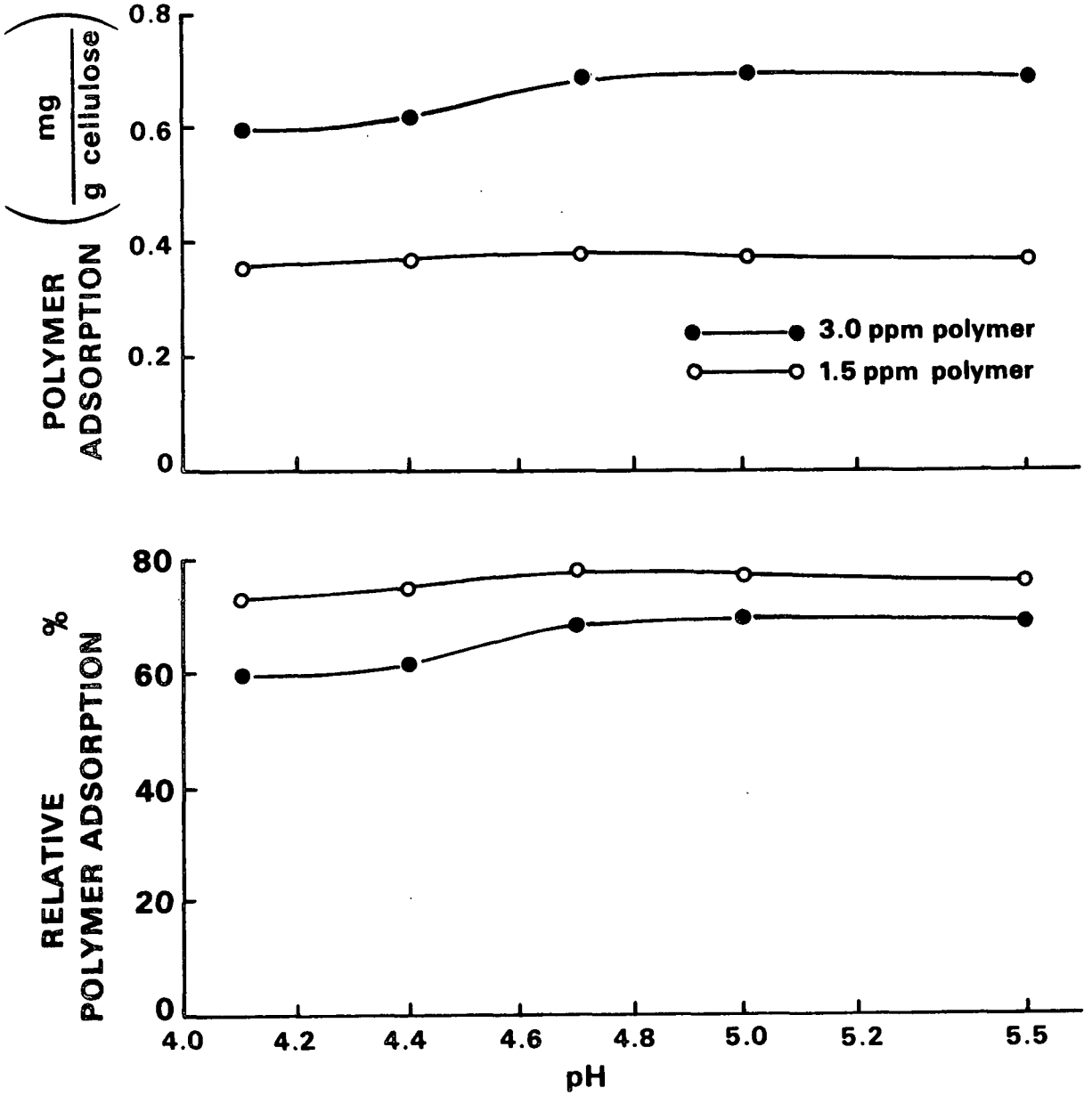

Figure 23. Top: Polymer adsorption as a function of pH and polymer concentration.
Bottom: Relative polymer adsorption as a function of pH and polymer concentration.

The effect of polymer concentration is also shown in Fig. 23. A doubling of the polymer concentration from 1.5 to 3.0 ppm almost doubles the amount of polymer adsorbed and slightly decreases the percent polymer adsorbed. From the equilibrium isotherm results one may expect polymer adsorption to double (i.e., same percent adsorption). However, the data in Fig. 23 were obtained under potentially nonequilibrium conditions in the presence of 0.01N KCl. Under the potentially nonequilibrium conditions there may be competition with the additional polymer or the potassium for adsorption onto the cellulose surface.

The effect of pH and adsorption time at 1.5 ppm polymer addition is presented in Fig. 24. An increase in adsorption time to 10 minutes causes a slight increase in the polymer adsorption. This indicates that the system isn't quite at equilibrium at 15 seconds adsorption time.

Effect of Polymer Concentration on Fiber Charge

The effect of polymer on fiber charge with and without KCl is presented in Fig. 25. Zeta potential is used as a measure of fiber charge. Apparently KCl reduces the negative charge on the fibers and increases the effect of polymer concentration. With KCl addition the fiber charge becomes reversed at approximately 3.0 ppm polymer. Without KCl the fiber charge remains highly negative and is less affected by polymer concentration. The reduction in relative adsorption with increasing polymer concentration (Fig. 23) may be explained by the effect of polymer concentration on fiber charge in 0.01N KCl. As the fiber charge becomes less negative, the relative polymer adsorption decreases.

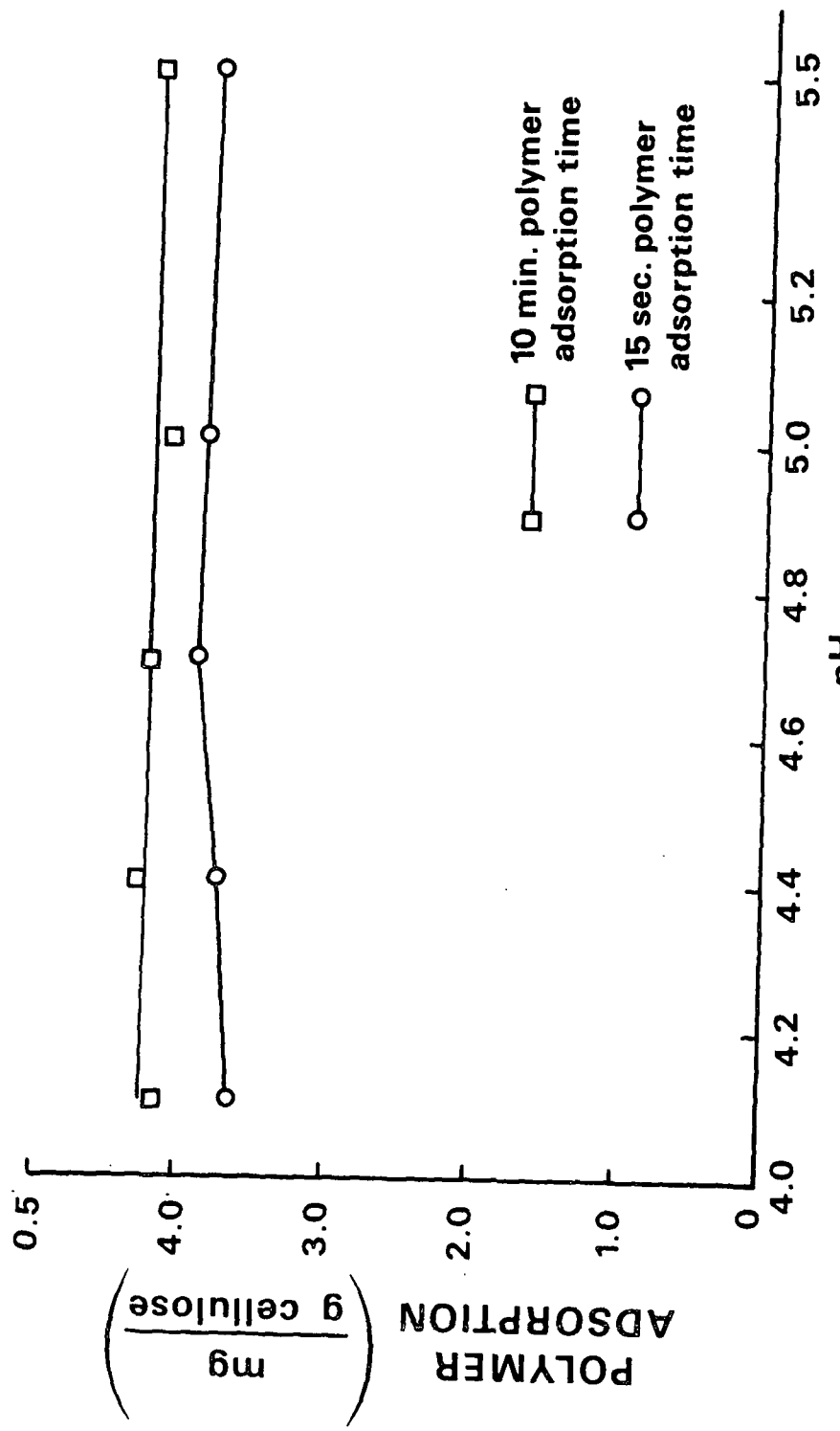

Figure 24. Polymer adsorption as a function of pH and polymer adsorption time.

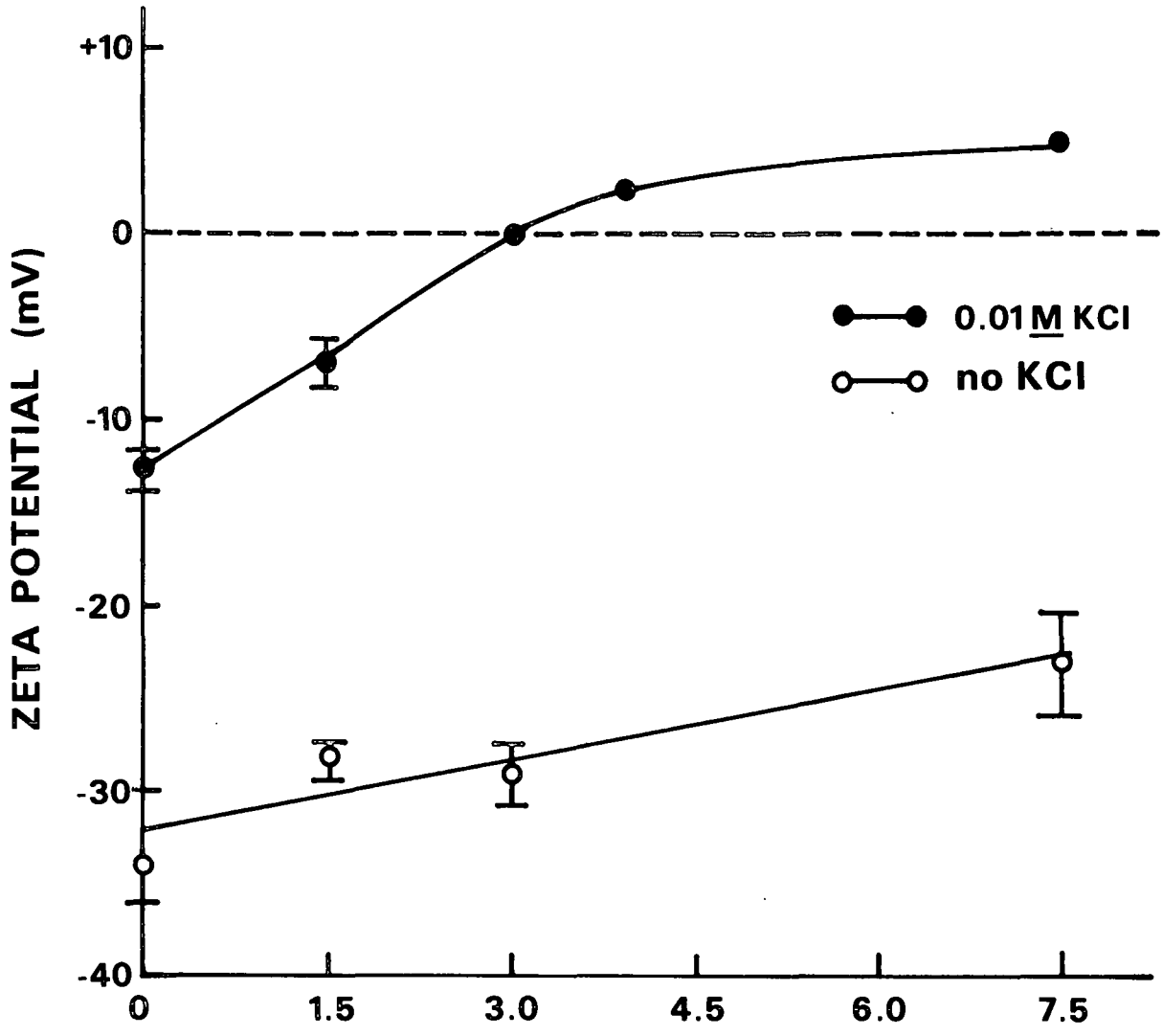

Figure 25. Zeta potential of the fibers as a function of potassium chloride concentration and polymer addition.

INFLUENCE OF POLYMER ON ALUMINUM ADSORPTION

The effect of polymer addition on aluminum adsorption is presented in Fig. 26-29. Figures 26 and 27 and Fig. 28 and 29 are for aluminum chloride and aluminum sulfate, respectively. Each point on the curves represents an average of two or three points. Only pairs of data (i.e., with and without polymer) obtained on the same day (i.e., same batch of pulp) are included. The highest polymer addition (i.e., 3.0 ppm) was used for Fig. 26-28. As seen in the figures, the difference in aluminum adsorption with and without polymer is insignificant.

INFLUENCE OF ALUMINUM ON POLYMER ADSORPTION

Effect of pH

The effect of pH and aluminum chloride on polymer adsorption at 2.5×10^{-4}M Al and 3.0 ppm polymer addition is presented in the top half of Fig. 30. For direct comparison, the polymer adsorption curve in the absence of aluminum (top half of Fig. 30) and the aluminum adsorption curve at 2.5×10^{-4}M Al (bottom half of Fig. 30) are included. The polymer adsorption is strongly dependent upon pH and aluminum chloride addition.

The effect of pH on polymer adsorption in the presence of aluminum chloride can be better examined by reference to two pH regions, one below the pHp where only soluble aluminum species exist, and one above the pHp where the aluminum precipitate is predominant. The lowest aluminum concentration was chosen for this example due to the extended soluble species region. Unfortunately, the actual pHp could not be accurately determined at this lowest aluminum concentration. However, when examining Fig. 16 (p. 55), one can confidently predict that the pHp lies somewhere between pH 4.6 and 4.7. Below the pHp where

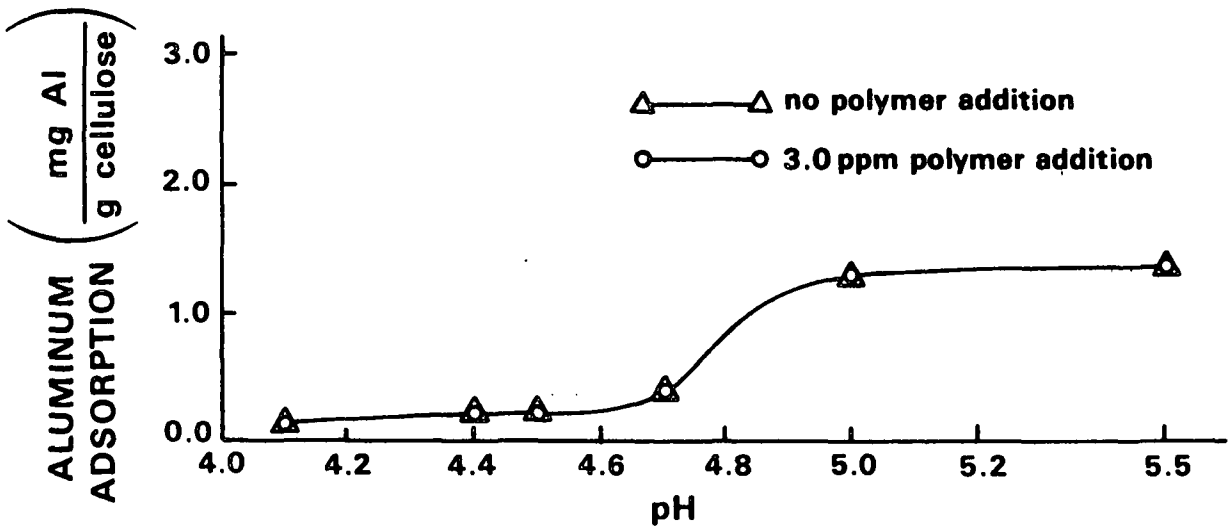

Figure 26. Aluminum adsorption as a function of polymer addition and pH for $AlCl_3$ (2.5×10^{-4}M Al).

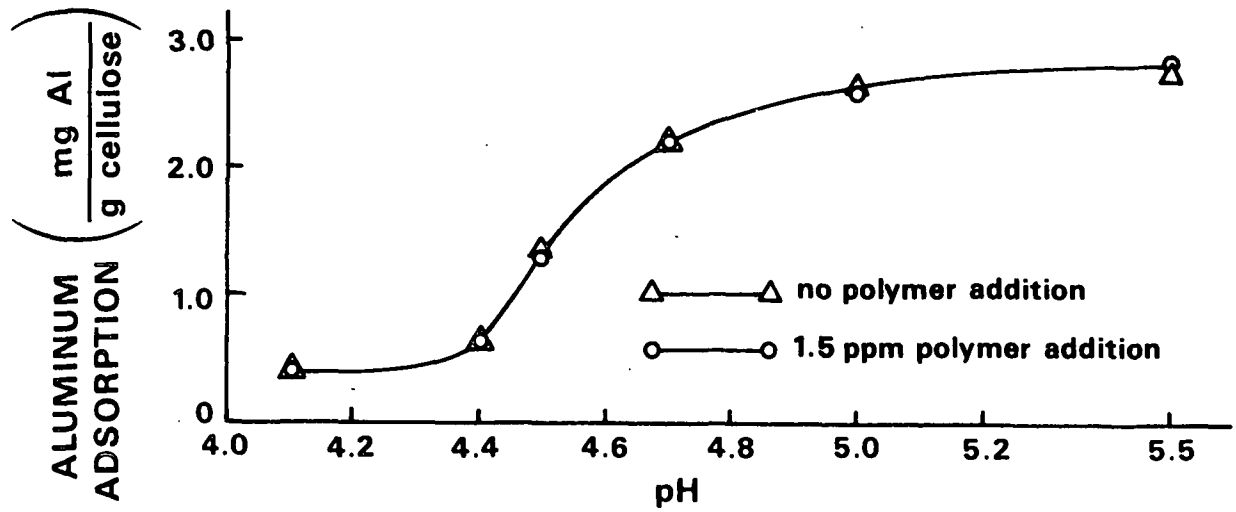

Figure 27. Aluminum adsorption as a function of polymer addition and pH for $AlCl_3$ (10.0×10^{-4}M Al).

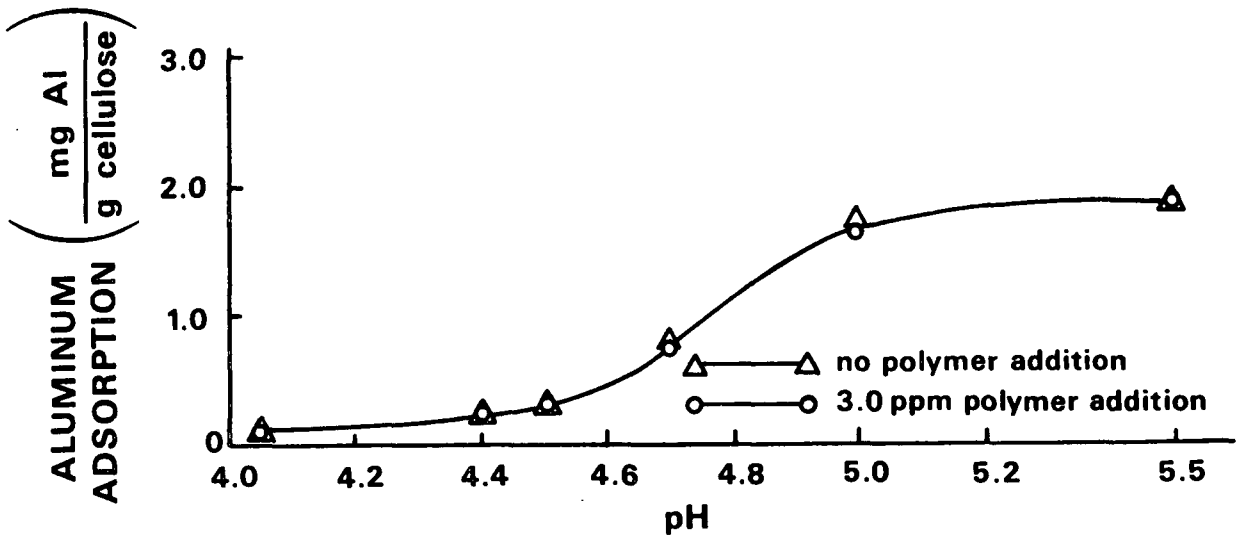

Figure 28. Aluminum adsorption as a function of polymer addition and pH for $Al_2(SO_4)_3$ (2.5×10^{-4} M Al).

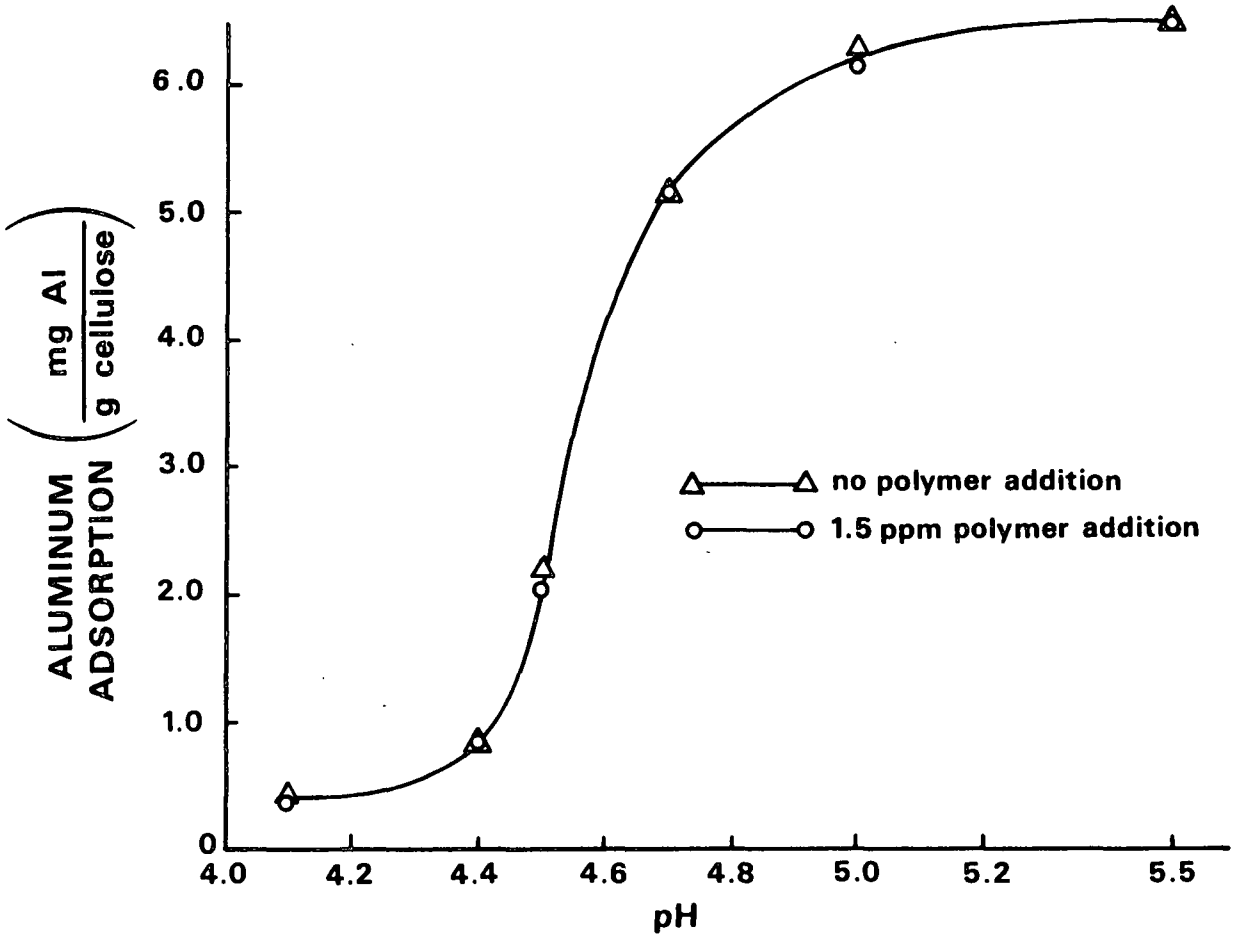

Figure 29. Aluminum adsorption as a function of polymer addition and pH for $Al_2(SO_4)_3$ (10.0×10^{-4} M Al).

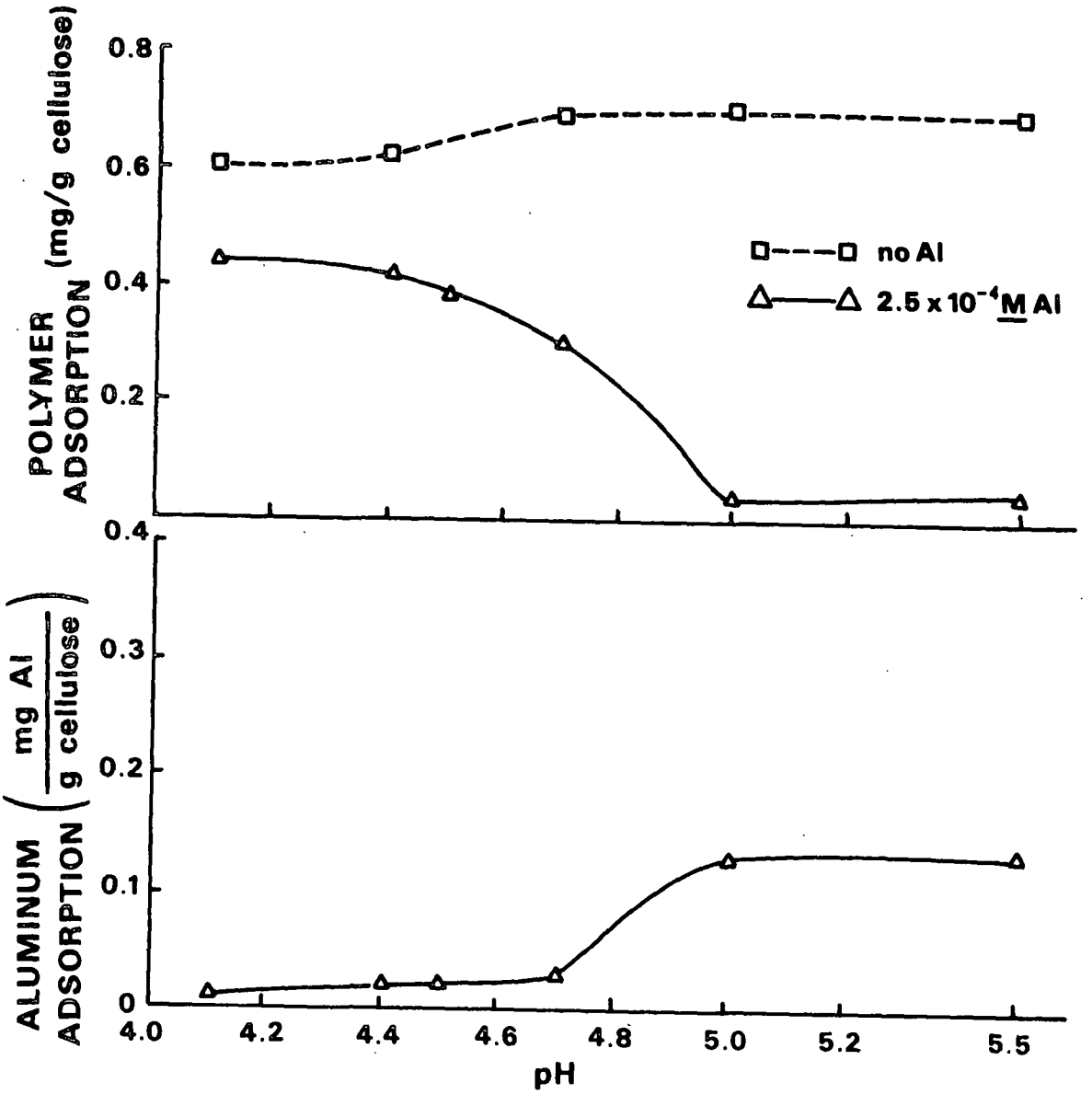

Figure 30. Top: Polymer adsorption as a function of pH in the presence of $AlCl_3$.
Bottom: Aluminum adsorption as a function of pH for $AlCl_3$ (2.5×10^{-4}M Al; 3.0 ppm polymer addition).

soluble aluminum species exist, polymer adsorption has been reduced but appears fairly independent of pH. Above the pHp as the precipitate is being formed the polymer adsorption drops rapidly to a very low but apparently constant value of approximately 0.05 mg/g cellulose (5% adsorption).

The effect of pH and aluminum sulfate on polymer adsorption at 2.5 x 10^{-4}M Al and 3.0 ppm polymer addition is presented in Fig. 31. Again, the polymer adsorption in the absence of aluminum and the aluminum adsorption at 2.5 x 10^{-4}M Al are included. Compared with the aluminum chloride results at this concentration, the polymer adsorption is less affected by pH and aluminum addition. The major difference occurs after the pHp where aluminum sulfate has a much less detrimental effect on polymer addition. However, below the pHp, where the soluble species exist, the two aluminum salts have a similar effect. In this region the polymer adsorption has been reduced but appears fairly independent of pH.

Effect of pH and Aluminum Concentration

The effect of pH and aluminum chloride concentration on polymer adsorption at 3.0 ppm polymer addition is presented in Fig. 32. Below the pHp there appears to be an inverse relationship between aluminum adsorption and polymer adsorption. That is, the increase in aluminum adsorption at higher aluminum concentrations appears to decrease the polymer adsorption. There is also a correlation between the drop in polymer adsorption and the pHp at the three aluminum concentrations. Above the pHp where the aluminum precipitate is predominant, the polymer adsorption drops to a level which is independent of aluminum concentration and pH.

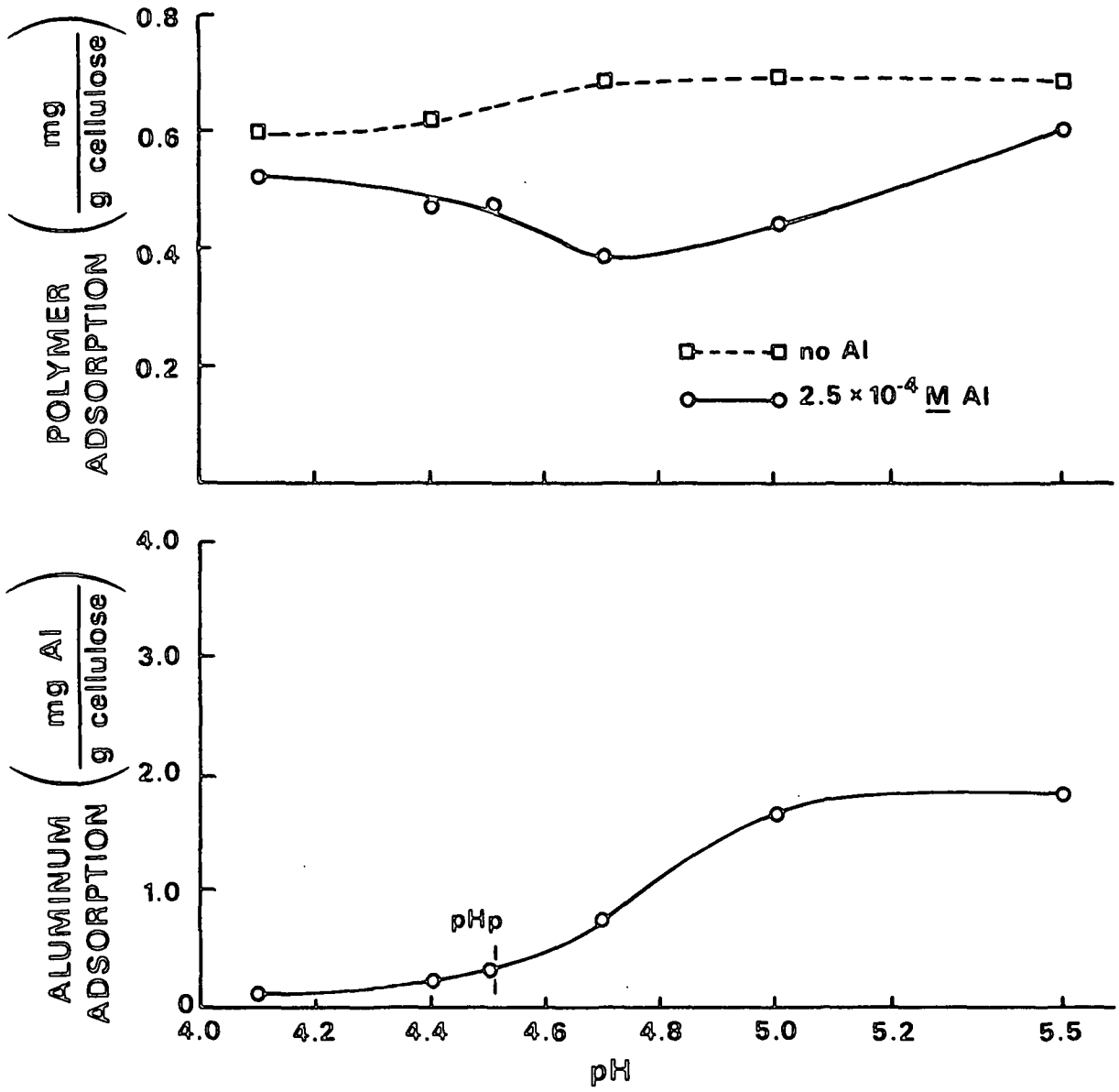

Figure 31. Top: Polymer adsorption as a function of pH in the presence of $Al_2(SO_4)_3$.
Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (2.5×10^{-4}M Al) (3.0 ppm polymer addition).

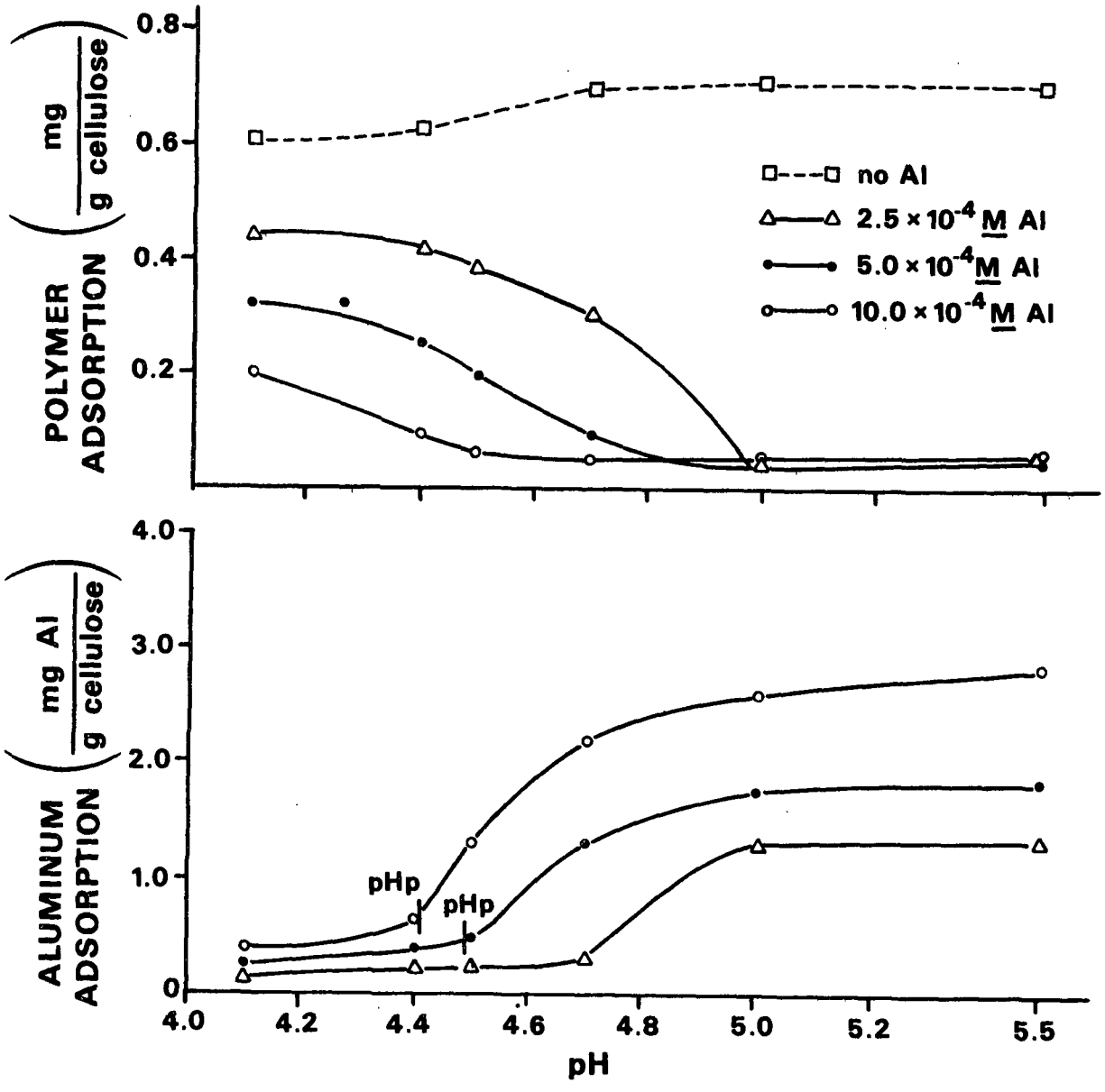

Figure 32. Top: Polymer adsorption as a function of pH and Al concentration in the presence of $AlCl_3$.
Bottom: Aluminum adsorption as a function of pH and Al concentration for $AlCl_3$ (3.0 ppm polymer addition).

The effect of pH and aluminum sulfate concentration on polymer adsorption at 1.5 ppm polymer addition and at 3.0 ppm polymer addition is presented in Fig. 33 and 34, respectively. Three interesting trends are present in the polymer adsorption curves: (1) Below the pHp an increase in aluminum concentration and adsorption lowers the polymer adsorption. This same relationship exists with aluminum chloride. (2) At high pH, 2.5×10^{-4}M Al is the most detrimental to polymer adsorption. As the aluminum concentration is increased from 2.5×10^{-4}M Al the polymer adsorption improves. This is unlike the effect of the aluminum chloride precipitate. (3) A minimum in polymer adsorption occurs just above the pHp. As with the pHp, this minimum in polymer adsorption shifts to a lower pH as the aluminum concentration is increased.

Effect of pH and Polymer Concentration

The effect of pH and polymer concentration in the presence of aluminum chloride is presented in Fig. 35. An increase in the polymer concentration from 1.5 ppm to 3.0 ppm increases the polymer adsorption (weight basis) throughout the pH range. However, the increase in polymer adsorption is very little at higher pH's. Figure 36 expresses the polymer adsorption as percent adsorption. The increase in polymer concentration lowers the percent adsorption by approximately 10% at the lower pH's.

The effect of pH and polymer concentration in the presence of aluminum sulfate is presented in Fig. 37-42. The effect of polymer concentration is similar throughout the pH range. This effect is similar to that observed at low pH's with aluminum chloride. First, an increase in the polymer concentration strongly increases the polymer adsorption throughout the pH range (Fig. 37-39). Second, the increase in polymer concentration lowers the percent adsorption

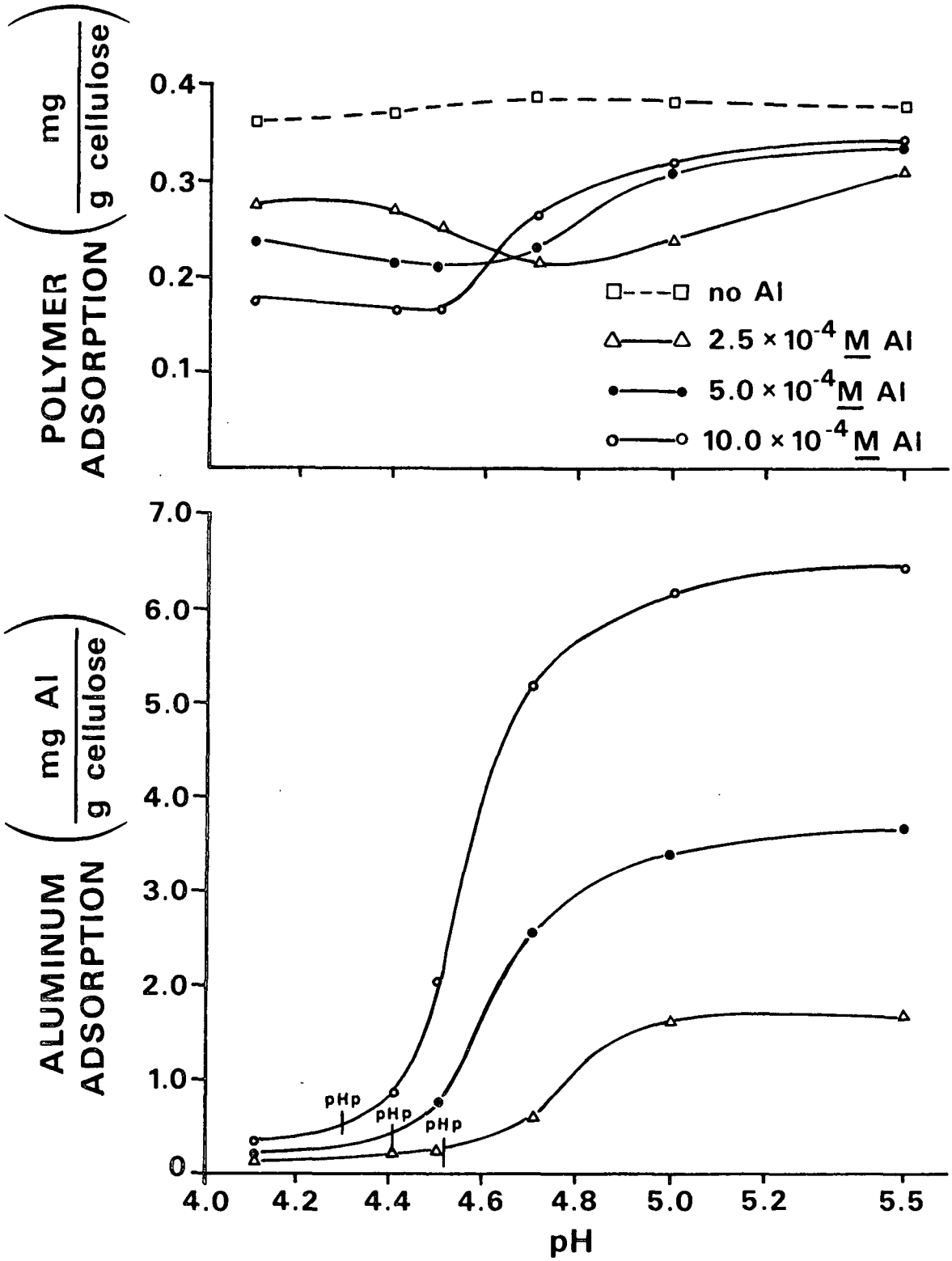

Figure 33. Top: Polymer adsorption as a function of pH and Al concentration in the presence of $Al_2(SO_4)_3$.
Bottom: Aluminum adsorption as a function of pH and Al concentration for $Al_2(SO_4)_3$ (1.5 ppm polymer addition).

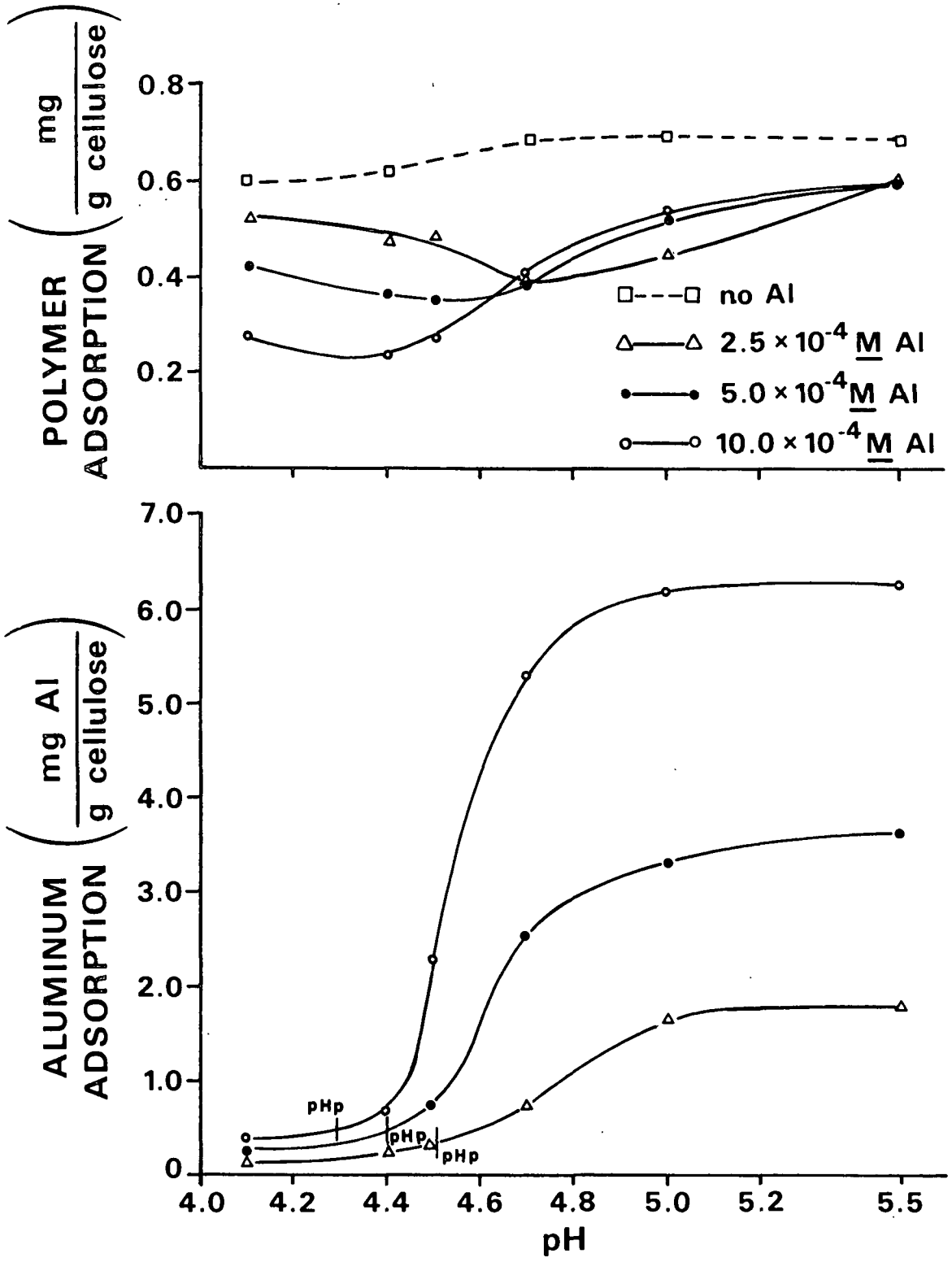

Figure 34. Top: Polymer adsorption as a function of pH and Al concentration in the presence of $Al_2(SO_4)_3$.
Bottom: Aluminum adsorption as a function of pH and Al concentration for $Al_2(SO_4)_3$ (3.0 ppm polymer addition).

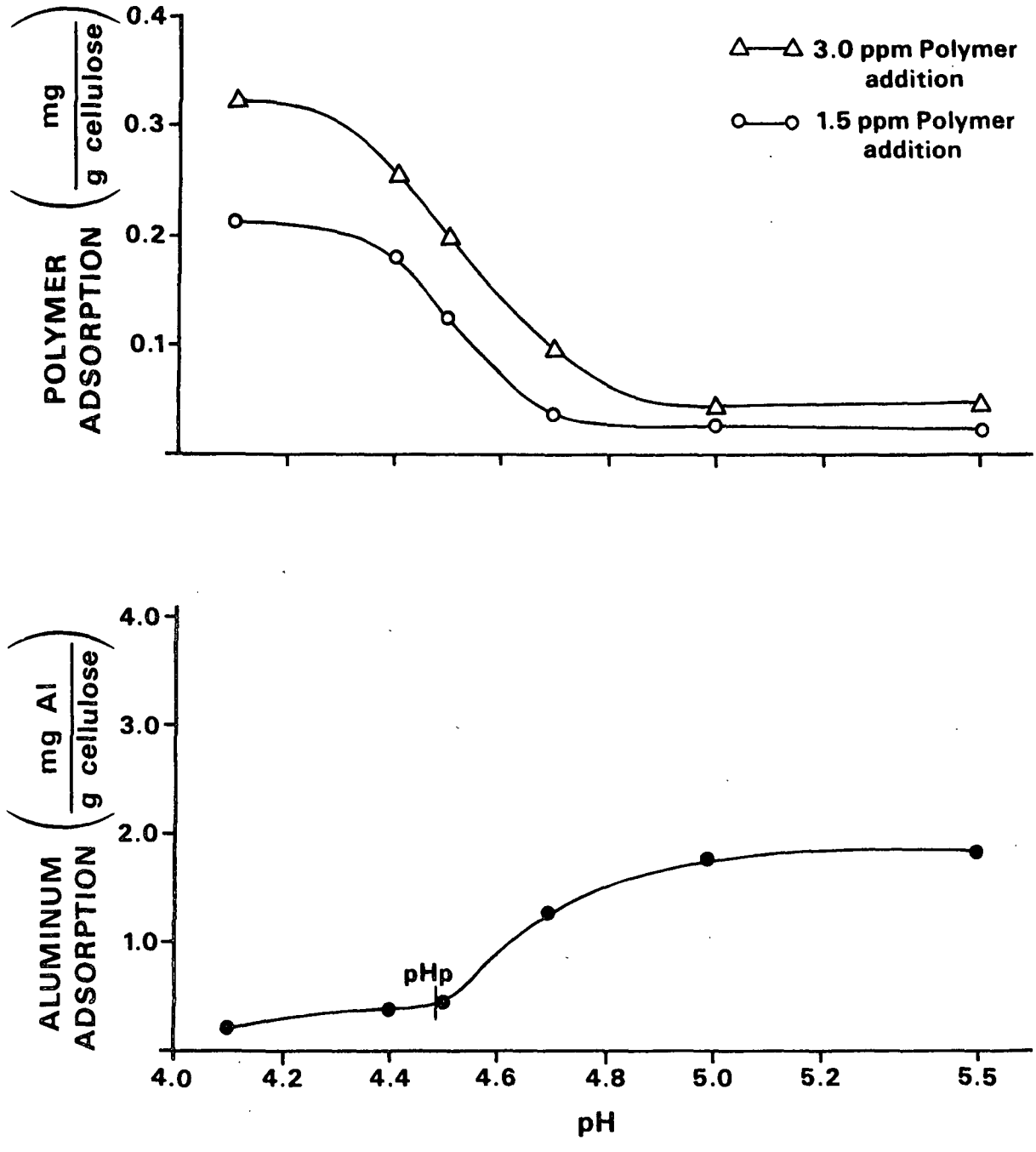

Figure 35. Top: Polymer adsorption as a function of pH and polymer addition in the presence of $AlCl_3$.
Bottom: Aluminum adsorption as a function of pH for $AlCl_3$ (5.0×10^{-4}M Al).

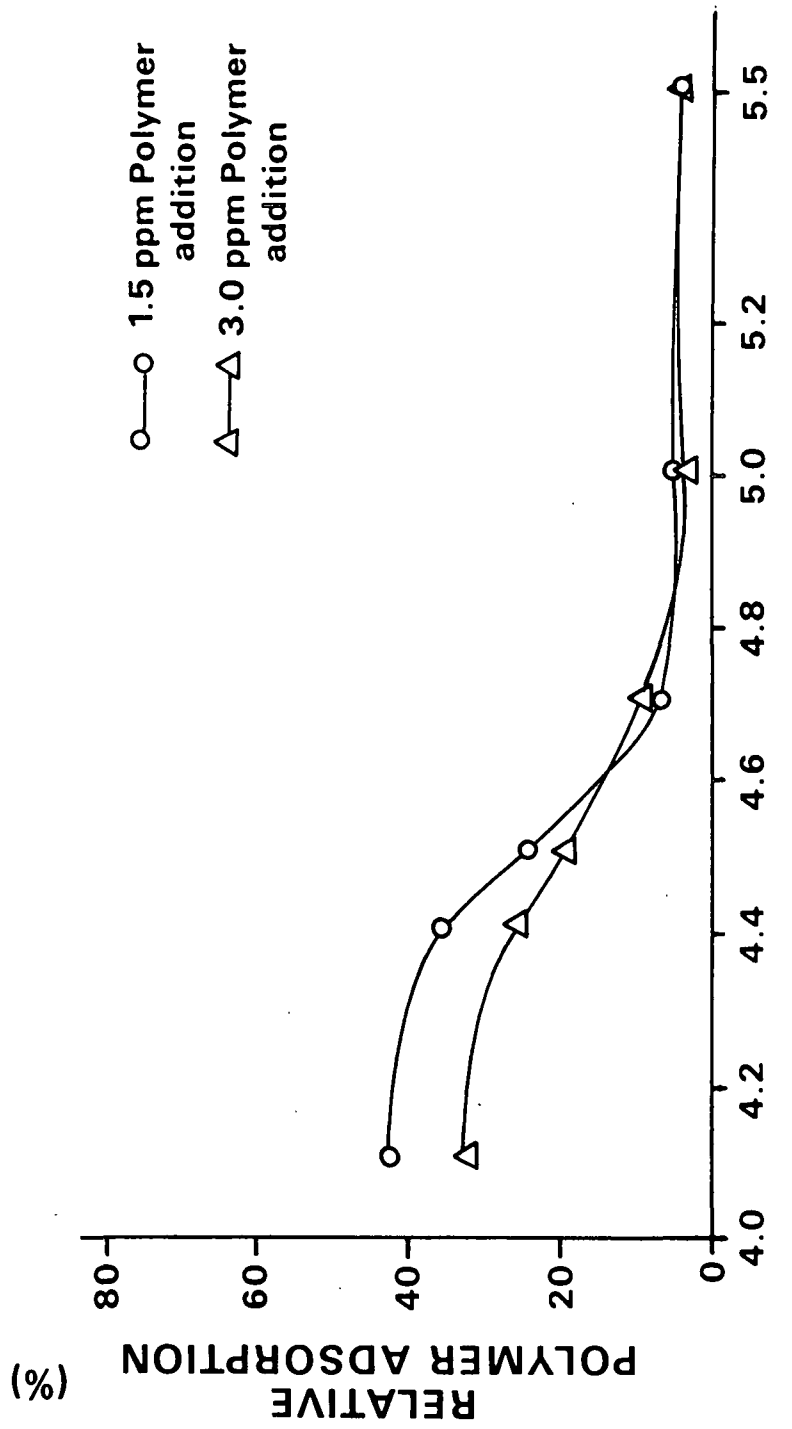

Figure 36. Relative polymer adsorption as a function of pH and polymer addition in the presence of $AlCl_3$ (5.0×10^{-4} M Al).

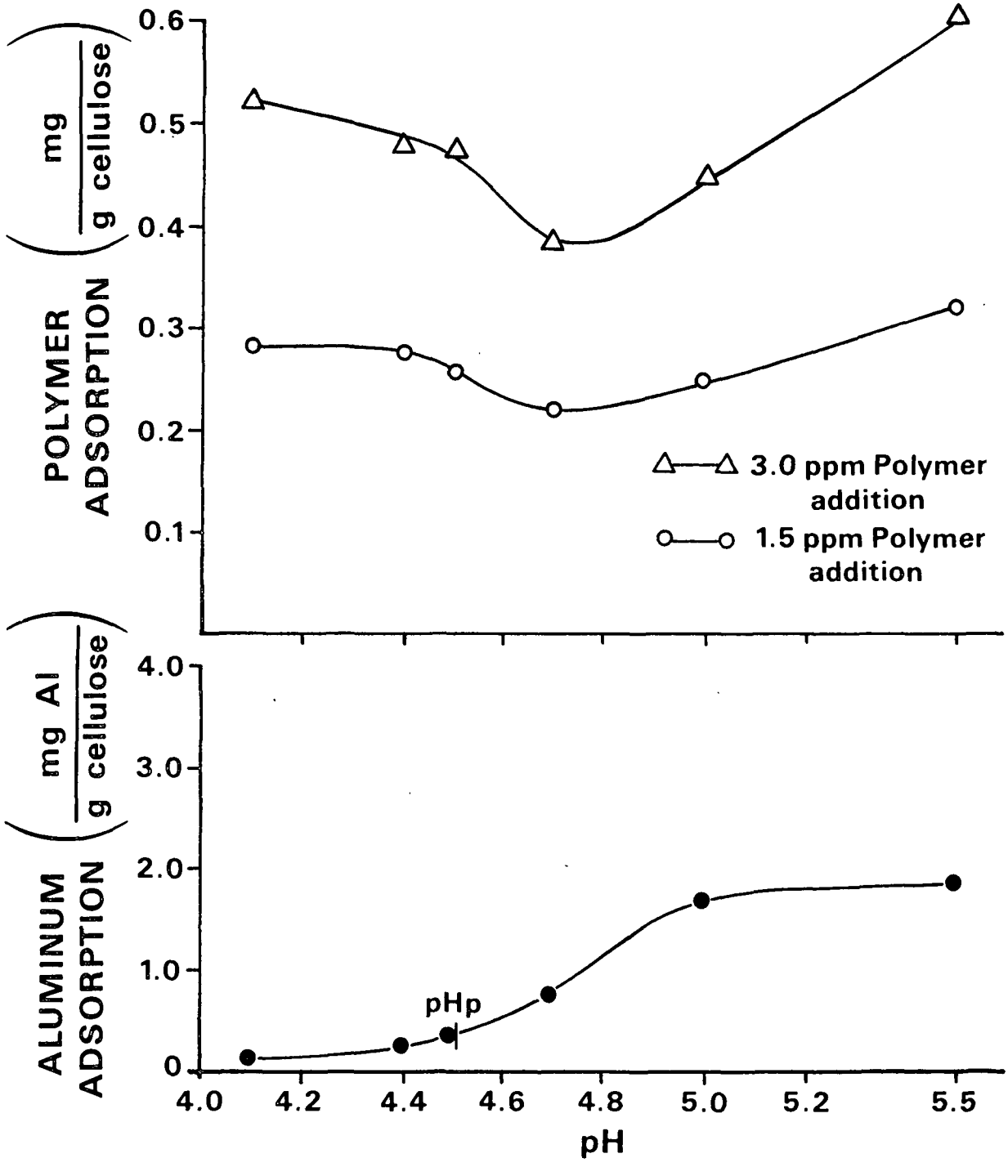

Figure 37. Top: Polymer adsorption as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$.
Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (2.5×10^{-4} M Al).

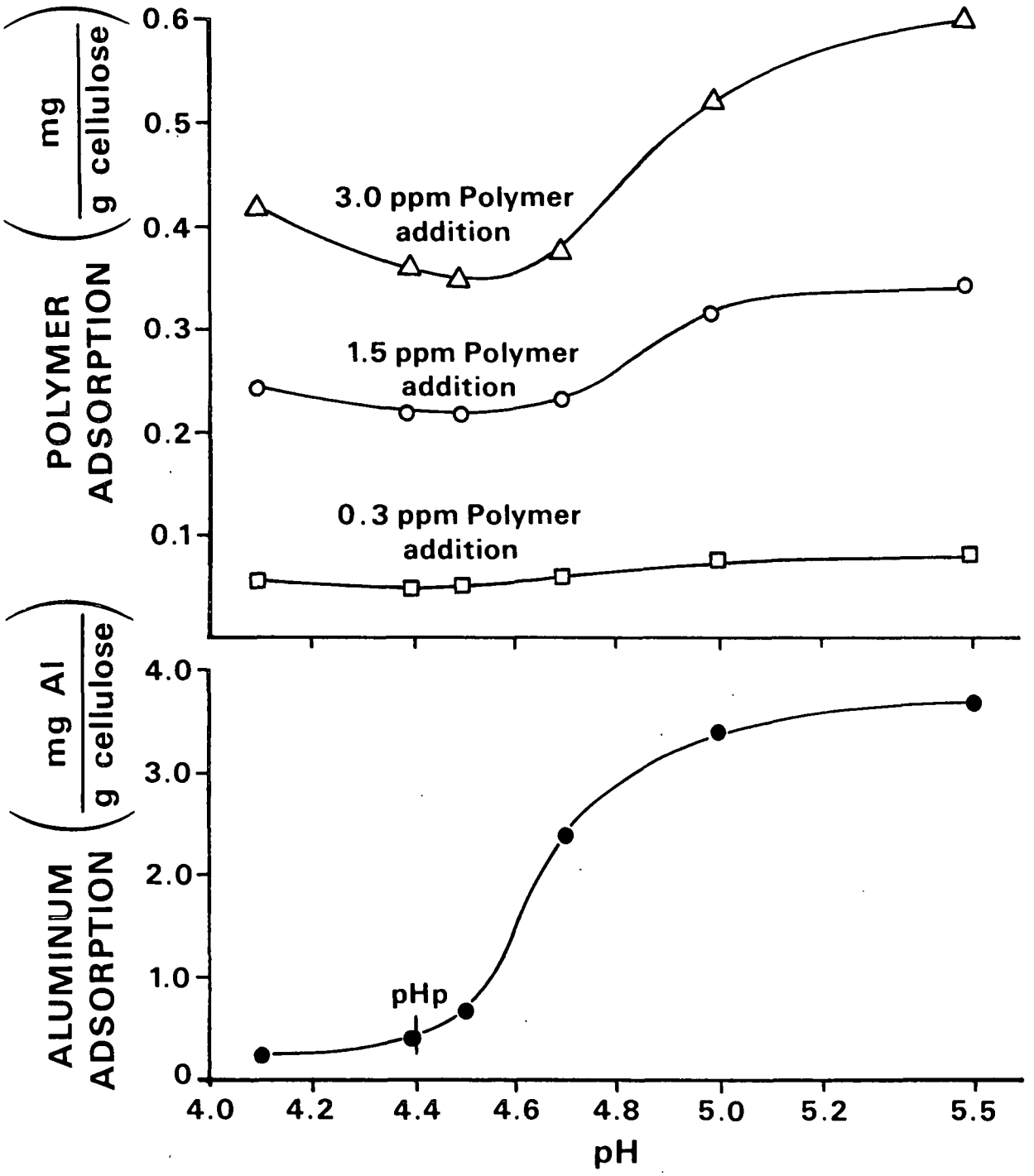

Figure 38. Top: Polymer adsorption as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$.
Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (5.0×10^{-4} M Al).

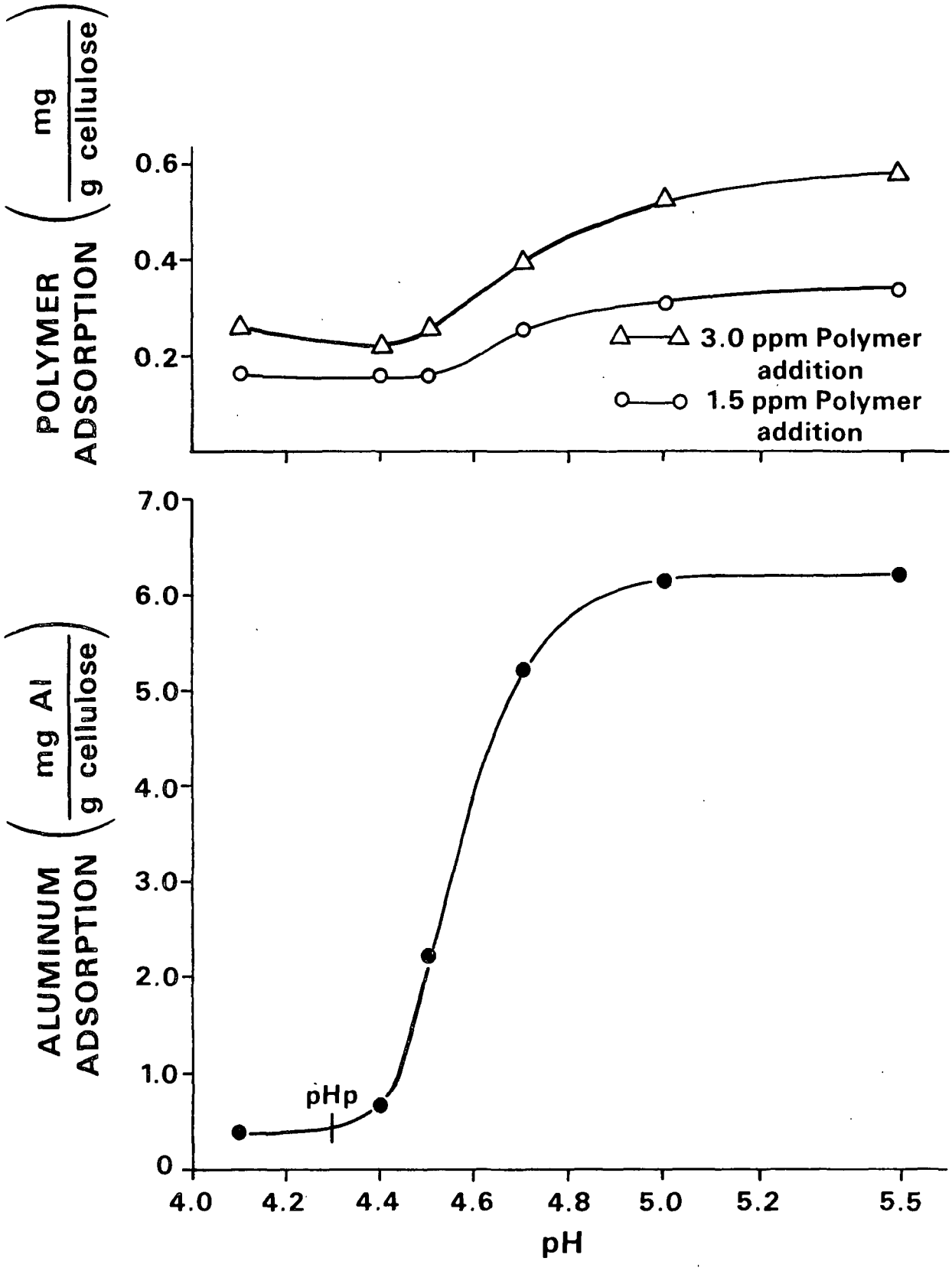

Figure 39. Top: Polymer adsorption as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$.
Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (10.0×10^{-4} M Al).

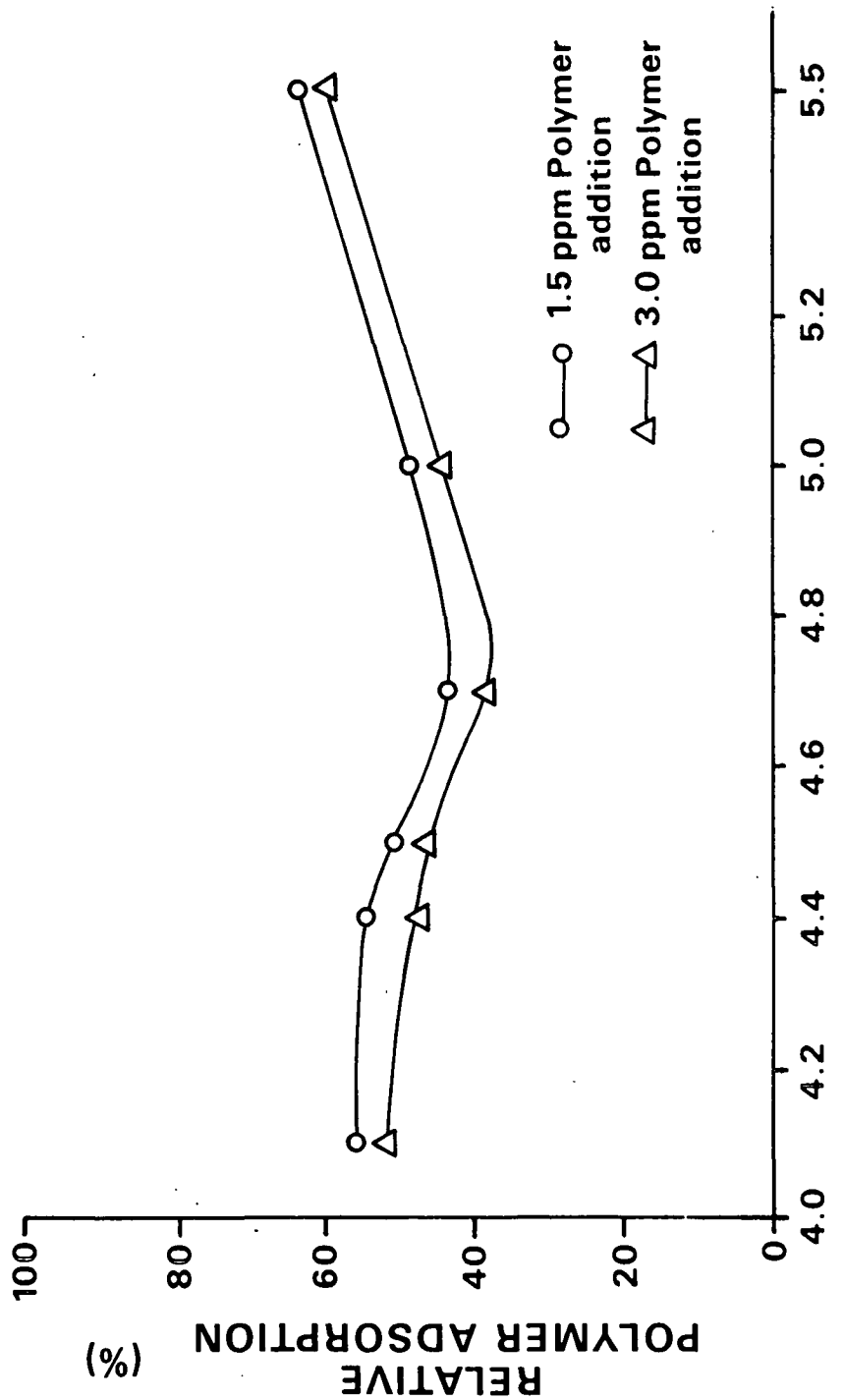

Figure 40. Relative polymer adsorption as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$ (2.5×10^{-4} M Al).

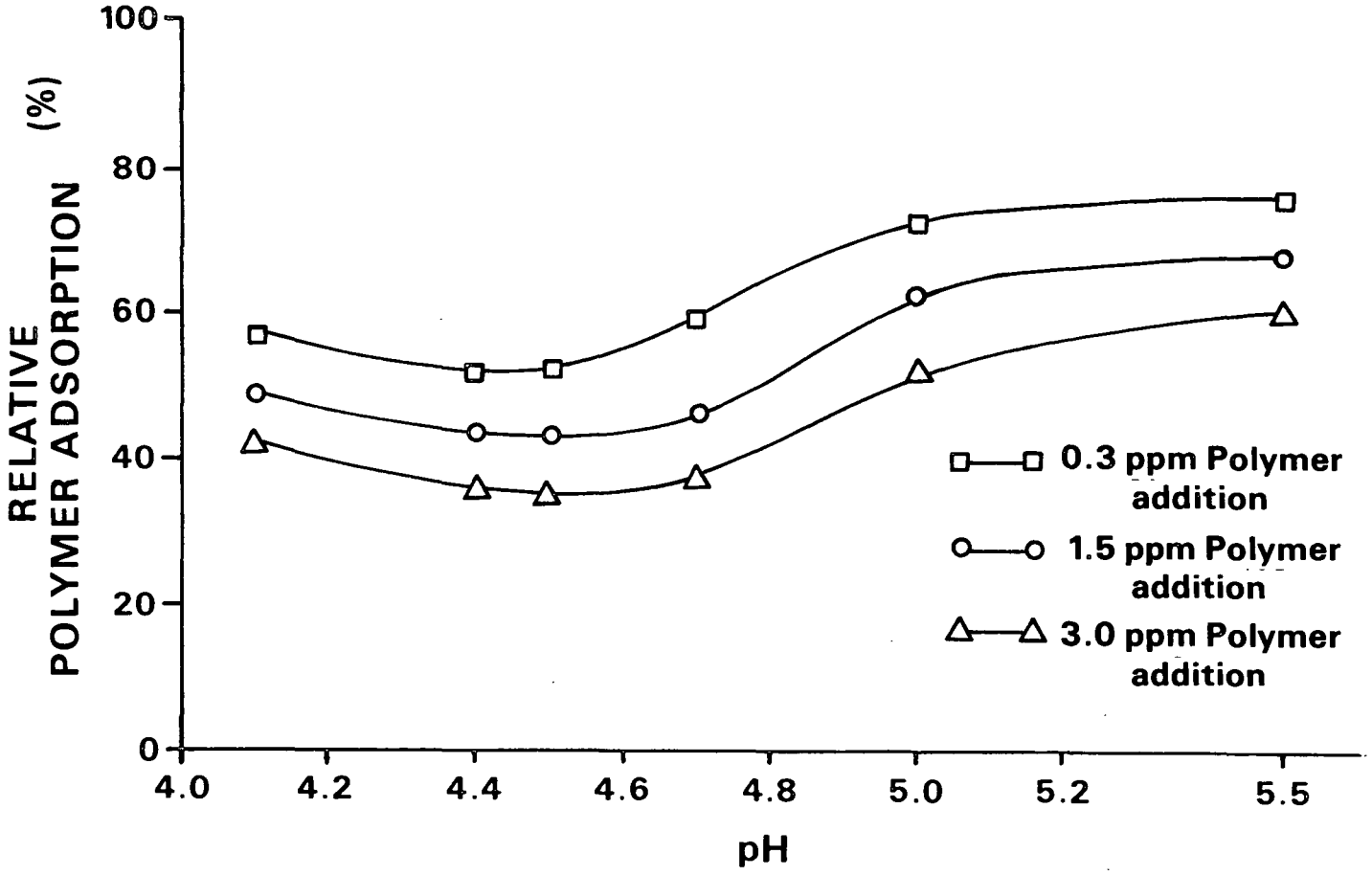

Figure 41. Relative polymer adsorption as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$ (5.0×10^{-4} M Al).

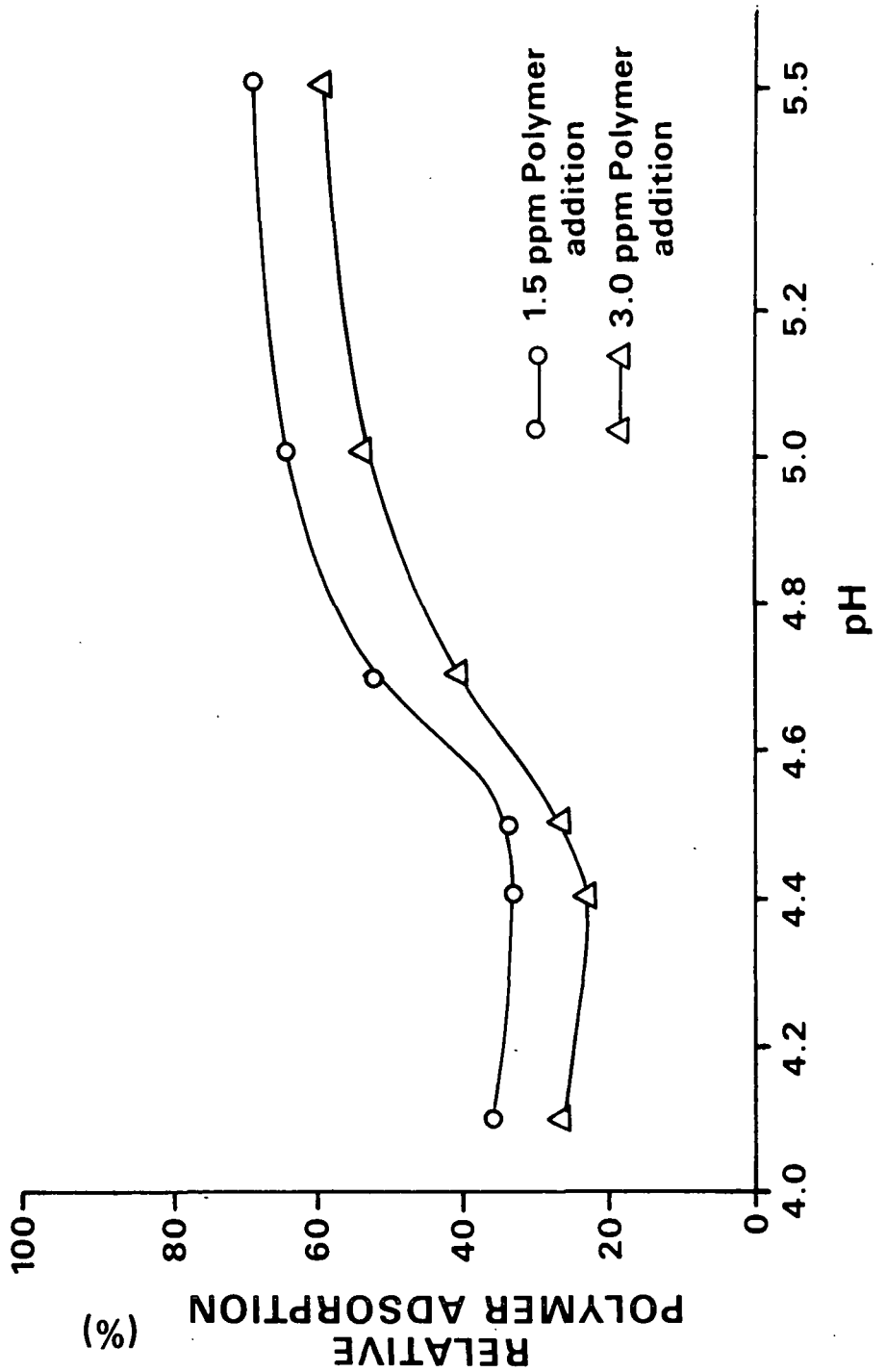

Figure 42. Relative polymer adsorption as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$ (10.0×10^{-4} M Al).

throughout the pH range (Fig. 40-42). The trends in percent adsorption with respect to pH remain identical at all polymer concentrations.

Effect of pH and Polymer Adsorption Time

The effect of pH and polymer adsorption time in the presence of aluminum chloride is presented in Fig. 43. An increase in the polymer adsorption time from 15 seconds to 10 minutes strongly increases the polymer adsorption at low pH's. In fact, at low pH and 10 minutes adsorption, aluminum has little effect on polymer adsorption. At high pH's very little improvement in polymer adsorption occurs with time. However, in terms of relative adsorption a 100% increase occurs. In both regions the increase in polymer adsorption with time indicates that the system is not in equilibrium at 15 seconds.

The effect of pH and polymer adsorption time in the presence of aluminum sulfate is presented in Fig. 44. The effect of adsorption time is similar throughout the pH range. This effect is similar to that observed at low pH's with aluminum chloride. First, an increase in adsorption time from 15 seconds to 10 minutes increases the polymer adsorption throughout the pH range. Second, aluminum sulfate has practically no effect on polymer adsorption throughout the pH range after 10 minutes. Again, this indicates that the system is not in equilibrium at 15 seconds.

Comparison of Aluminum Sulfate to Aluminum Chloride

The similarities and differences between the effects of the two aluminum salts can be better understood with Fig. 45-48. Figure 45 compares the two aluminum salts at 5.0×10^{-4}M Al and 1.5 ppm polymer addition. Figures 46 to 48 compare the two aluminum salts at concentrations ranging from 2.5×10^{-4}M Al to 10.0×10^{-4}M Al at 3.0 ppm polymer addition. Below the pHp's, where the soluble

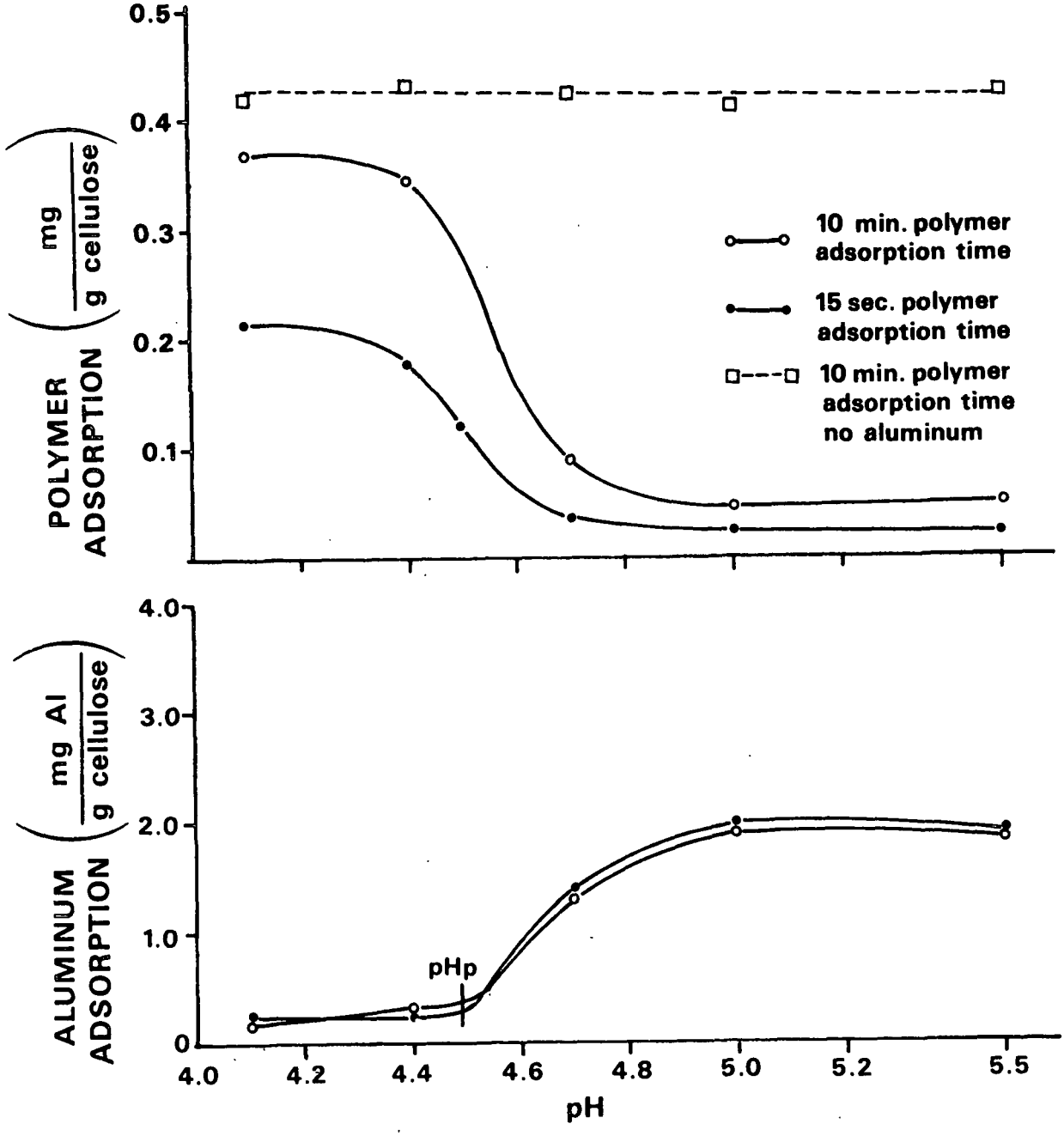

Figure 43. Top: Polymer adsorption as a function of pH and polymer adsorption time in the presence of $AlCl_3$.
Bottom: Aluminum adsorption as a function of pH for $AlCl_3$ (5.0×10^{-4} M Al; 1.5 ppm polymer addition).

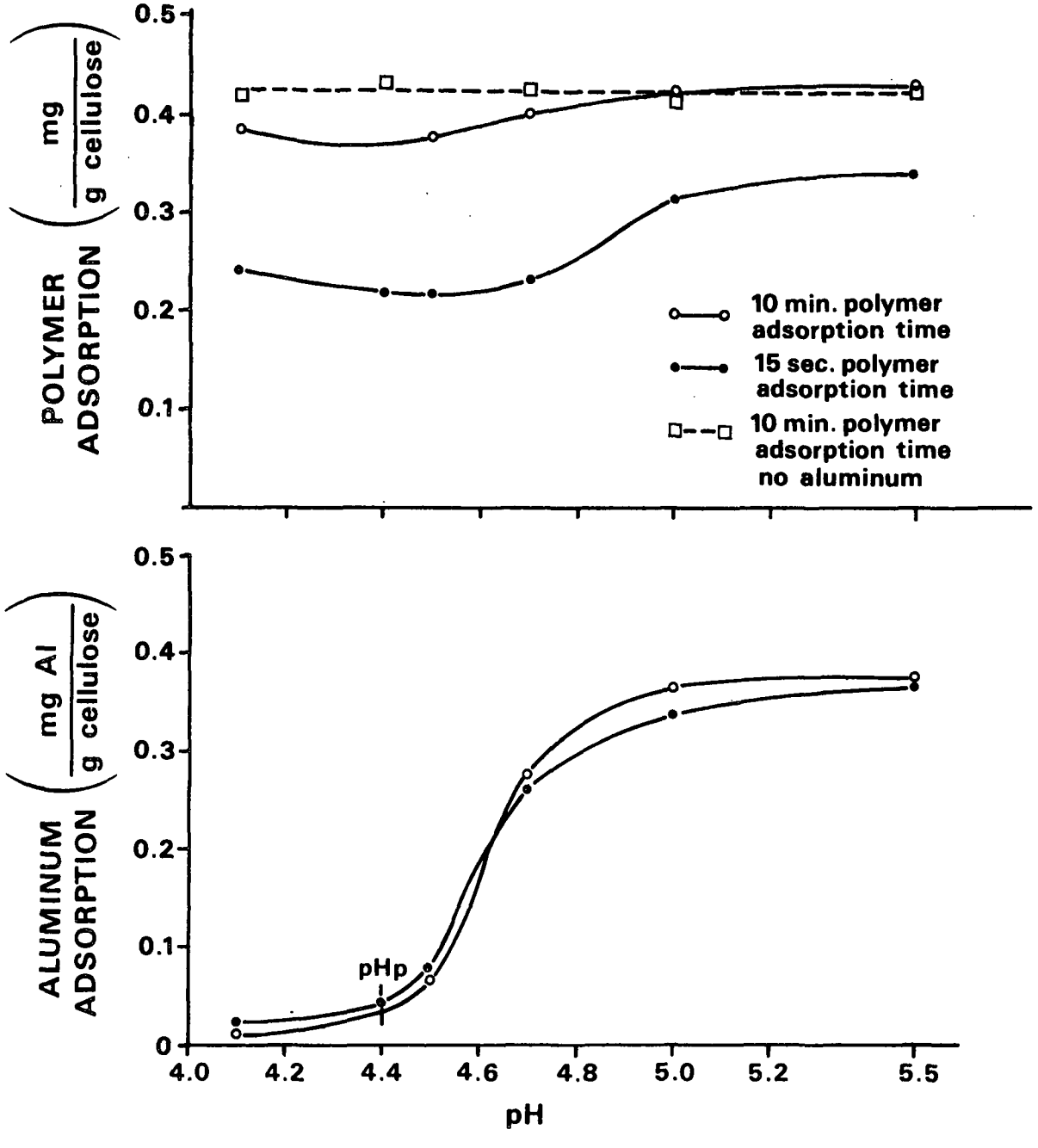

Figure 44. Top: Polymer adsorption as a function of pH and polymer adsorption time in the presence of $Al_2(SO_4)_3$.
Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (5.0×10^{-4} M Al; 1.5 ppm polymer addition).

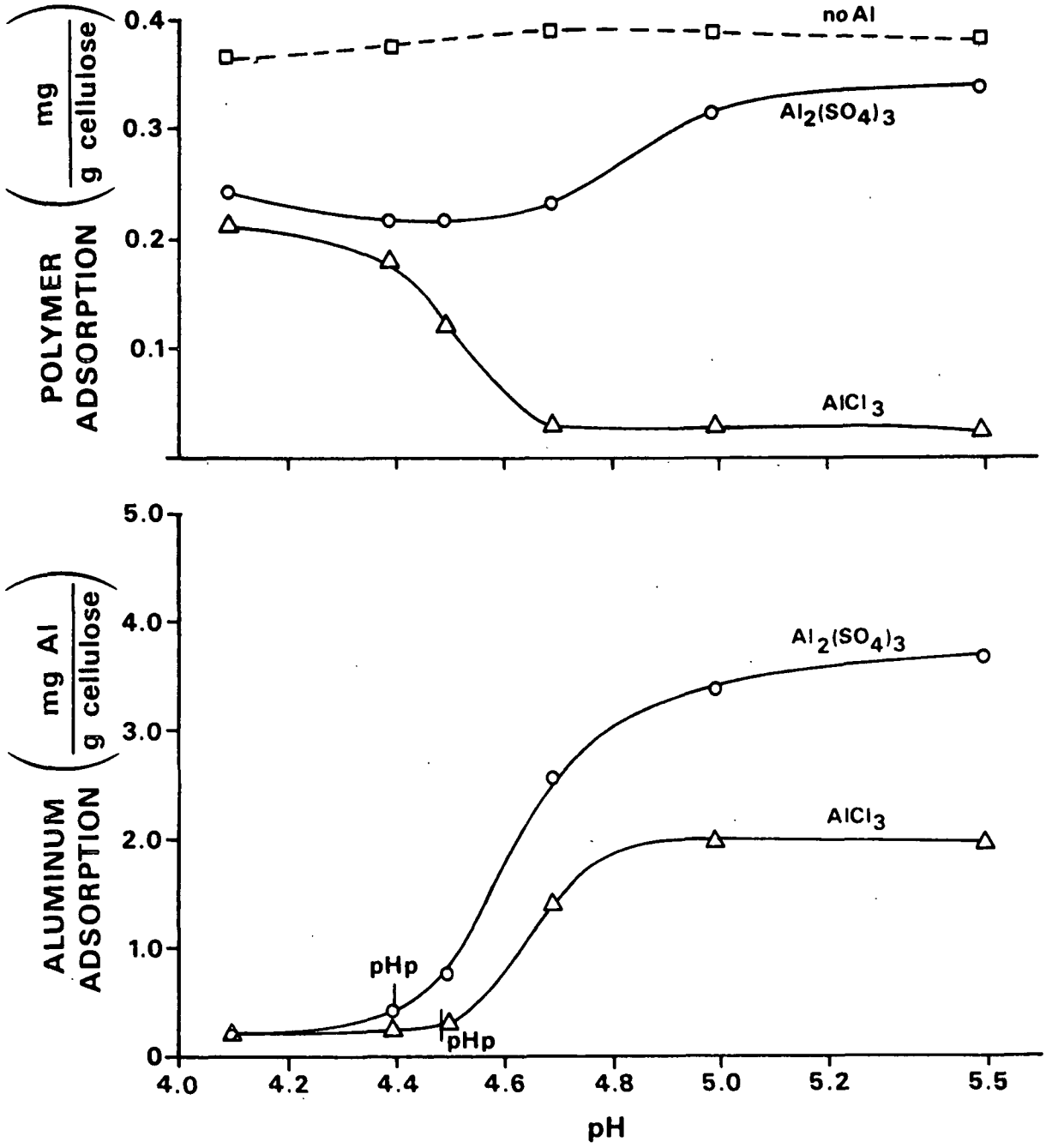

Figure 45. Top: Polymer adsorption as a function of pH and aluminum salt.
Bottom: Aluminum adsorption as a function of pH and aluminum salt (5.0×10^{-4} M Al; 1.5 ppm polymer addition).

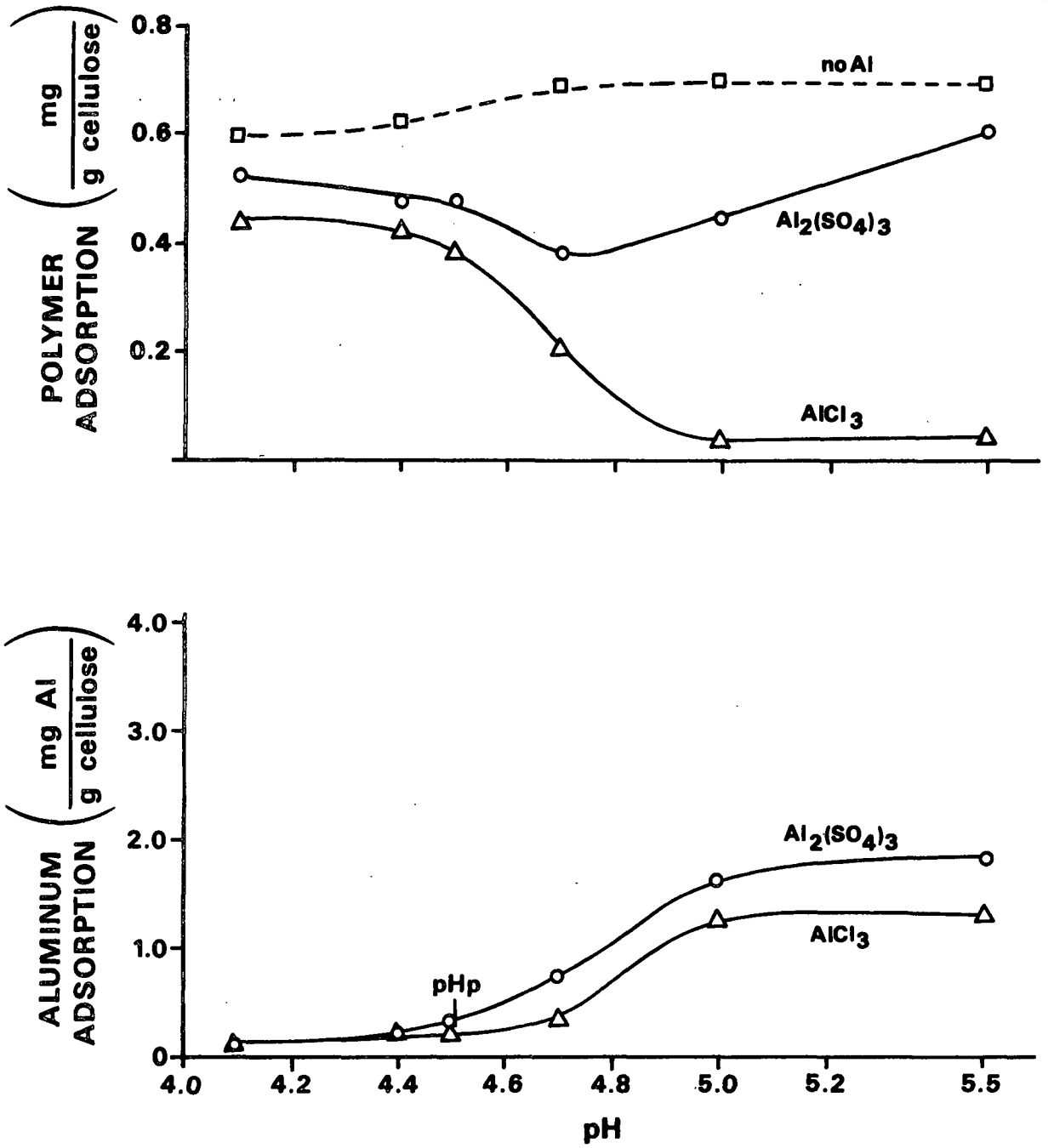

Figure 46. Top: Polymer adsorption as a function of pH and aluminum salt.
Bottom: Aluminum adsorption as a function of pH and aluminum salt (2.5×10^{-4} M Al; 3.0 ppm polymer addition).

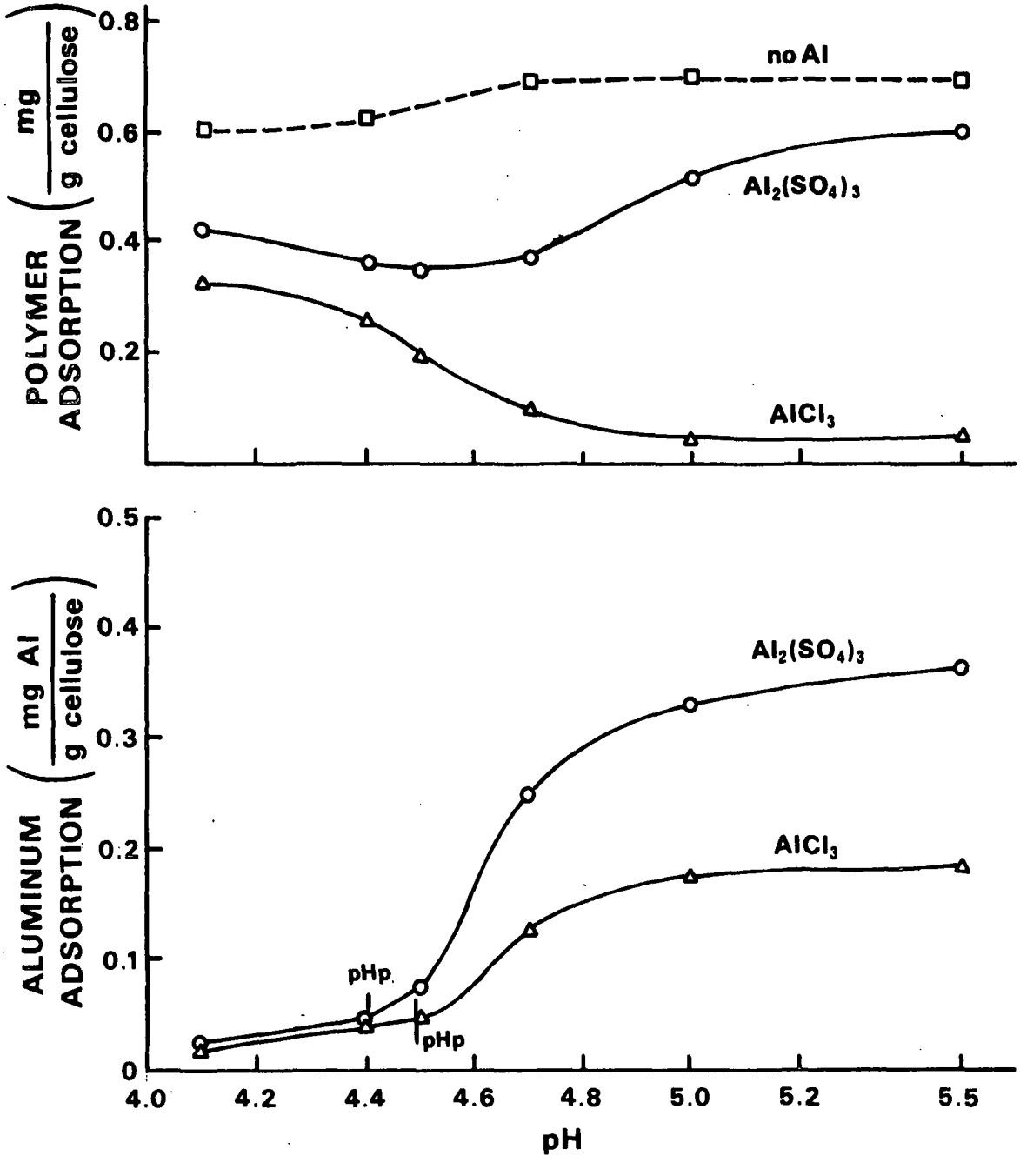

Figure 47. Top: Polymer adsorption as a function of pH and aluminum salt.
Bottom: Aluminum adsorption as a function of pH and aluminum salt (5.0×10^{-4} M Al; 3.0 ppm polymer addition).

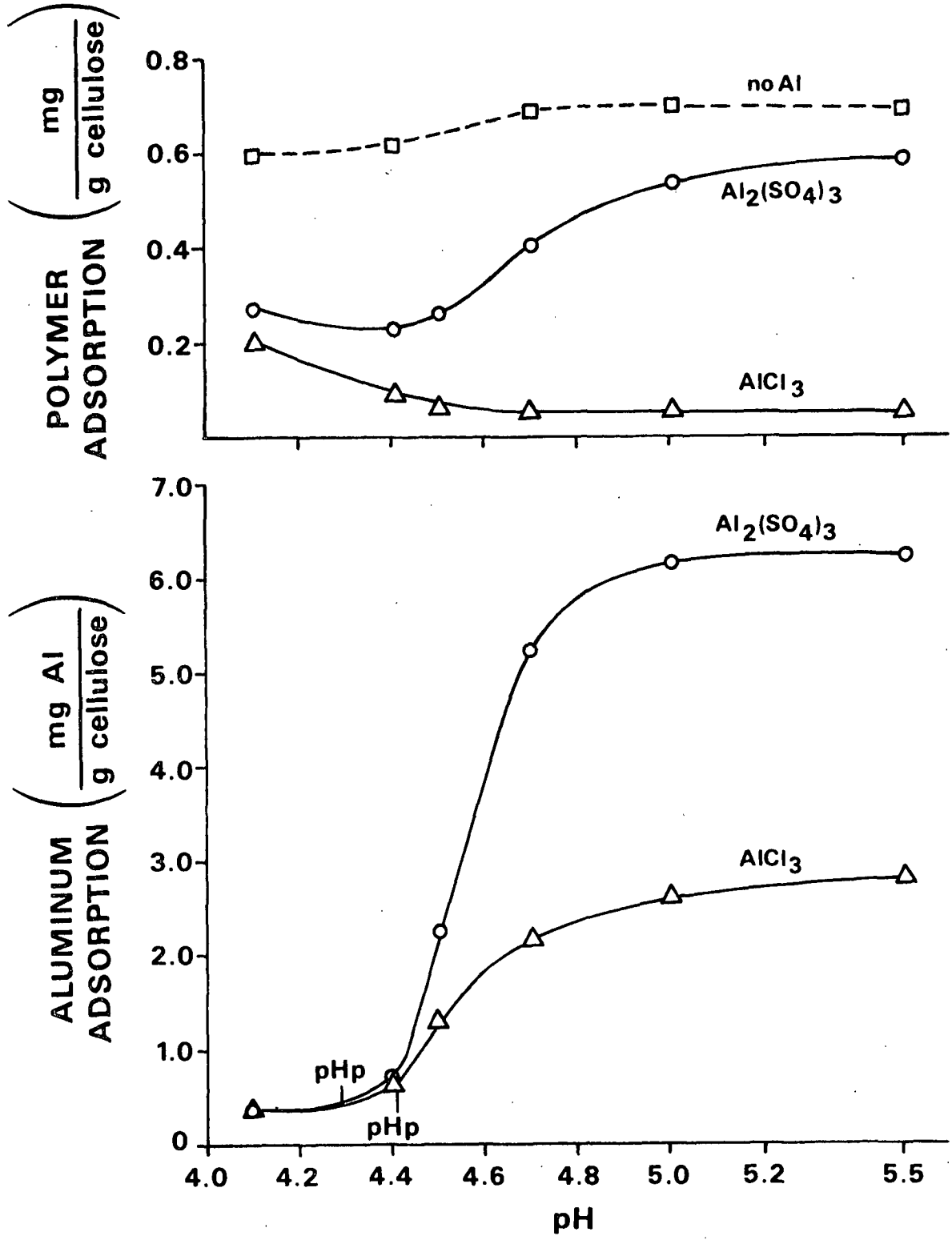

Figure 48. Top: Polymer adsorption as a function of pH and aluminum salt.
Bottom: Aluminum adsorption as a function of pH and aluminum salt (10.0×10^{-4}M Al; 3.0 ppm polymer addition).

aluminum species exist, the effects of the two aluminum salts are very similar; however, aluminum chloride causes a slightly greater reduction in polymer adsorption. As the vicinity of the pHp's is approached, both curves start to drop. In this area both soluble and insoluble aluminum species may exist together. However, soon after the pHp's the two aluminum salts contrast sharply. The aluminum chloride precipitate reduces the polymer adsorption to an extremely low level, whereas the aluminum sulfate precipitate has little effect on polymer adsorption.

Summary of Polymer Adsorption Trends

Objectives 1 and 2 have been accomplished by the preceding sections. Objective 1 was to determine whether aluminum salts influence polymer adsorption. Objective 2 was to establish the conditions by which this influence can occur. Accomplishing these objectives has revealed several major trends in polymer adsorption.

The first trend occurs with both aluminum salts, below the pHp in the region where only soluble aluminum species exist. In this region polymer adsorption is dependent upon the concentration of aluminum (Fig. 32-34). As the aluminum concentration increases, the aluminum adsorption increases and the polymer adsorption decreases.

The second trend is a minimum in polymer adsorption which occurs close to the pHp in the presence of aluminum sulfate. An increase in the pHp when increasing aluminum concentration causes a corresponding increase in the pH at which the minimum occurs. The same trend may be present with aluminum chloride; however, the trend, if it exists, cannot clearly be separated from the large reduction in polymer adsorption that occurs above the pHp.

The third trend is the large reduction in polymer adsorption that occurs above the pHp with aluminum chloride. In this region the polymer adsorption decreases to a very low level of approximately 5% adsorption.

The final major trend is the high polymer adsorption which exists with aluminum sulfate at high pH's. In this region the aluminum precipitate is predominant. However, unlike aluminum chloride, the aluminum sulfate precipitate has only a small detrimental effect on polymer adsorption. The aluminum sulfate precipitate is the most detrimental at 2.5×10^{-4}M Al (Fig. 33 and 34, p. 81 and 82). Above this concentration the precipitate becomes less detrimental.

Investigation of Mechanisms

Additional experiments have been conducted to determine the mechanisms by which aluminum salts influence polymer adsorption.

Effect of Aluminum Salt Anions

The possible effects of the aluminum salt anions at various concentrations are presented in Fig. 49. The concentration range of each anion corresponds to that existing in the presence of their respective aluminum salts from no aluminum to 10.0×10^{-4}M Al. Chloride and sulfate anions were added in the form of KCl and K_2SO_4 to stock containing 0.01N KCl in the absence of aluminum. A pH of 4.1 was chosen for all tests.

The potassium salts of the anions appear to have a small, but measurable detrimental effect on polymer adsorption. It was impossible to exclude the effect of the potassium on the polymer adsorption; however, these results should represent the maximum possible effect of the anions. K_2SO_4 appears to have twice the effect on polymer adsorption, but contains twice the concentration of potassium. Whether the detrimental effect is due to potassium or the

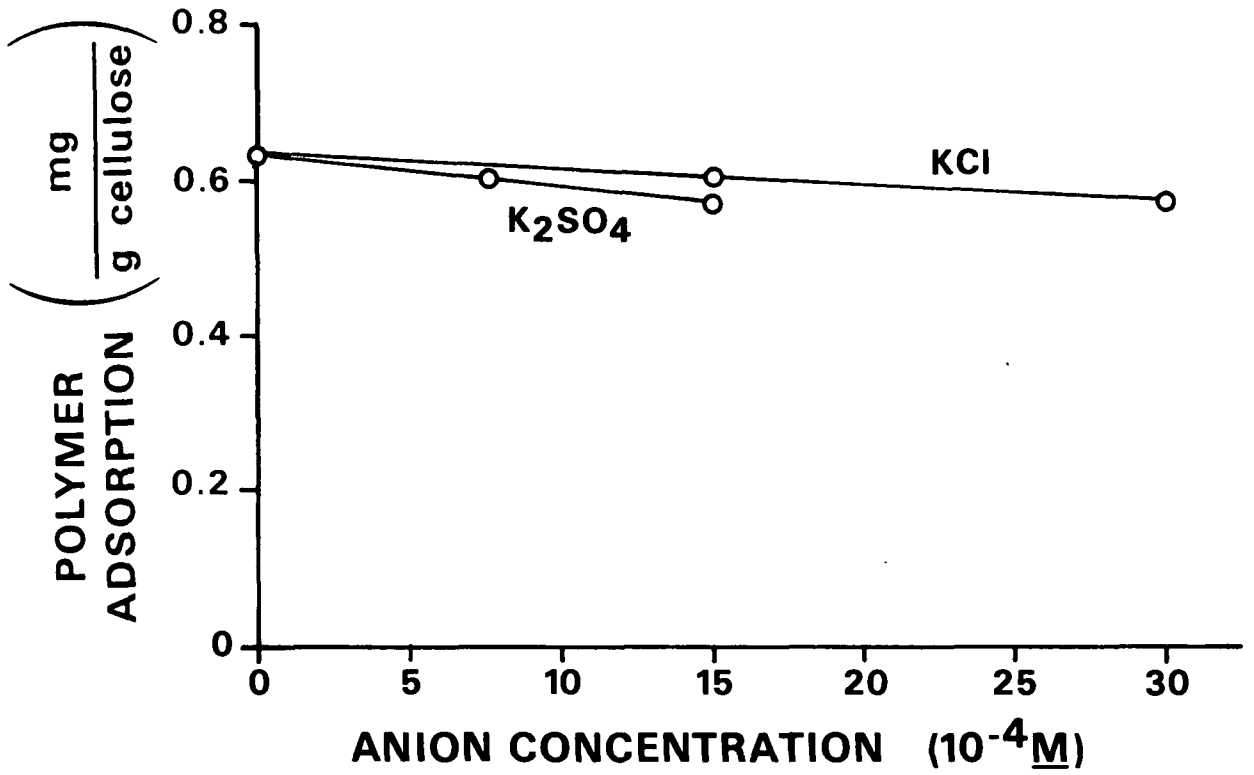

Figure 49. Polymer adsorption as a function of anion concentration (3.0 ppm polymer addition; pH = 4.4; 0.01N KCl background).

anions is unimportant since the effect is too small to account for the observed differences in polymer adsorption.

Effect of Cation Valence and Concentration

The effects of cations at various valences and concentrations are presented in Fig. 50. Chloride salts of potassium, calcium, and lanthanum were used to illustrate the effect of valence. Lanthanum was chosen as the trivalent ion since it remains unhydrolyzed up to a pH of 8. This excludes any possibility of trace amounts of precipitate. Concentrations were chosen to match the cation concentrations produced by the aluminum salts at 5.0×10^{-4}M and 10.0×10^{-4}M Al. All cations were added to stock containing 0.01N KCl in the absence of aluminum. A pH of 4.1 was chosen for all tests. For comparison the effects of aluminum chloride and aluminum sulfate at pH 4.1 are represented by dashed curves.

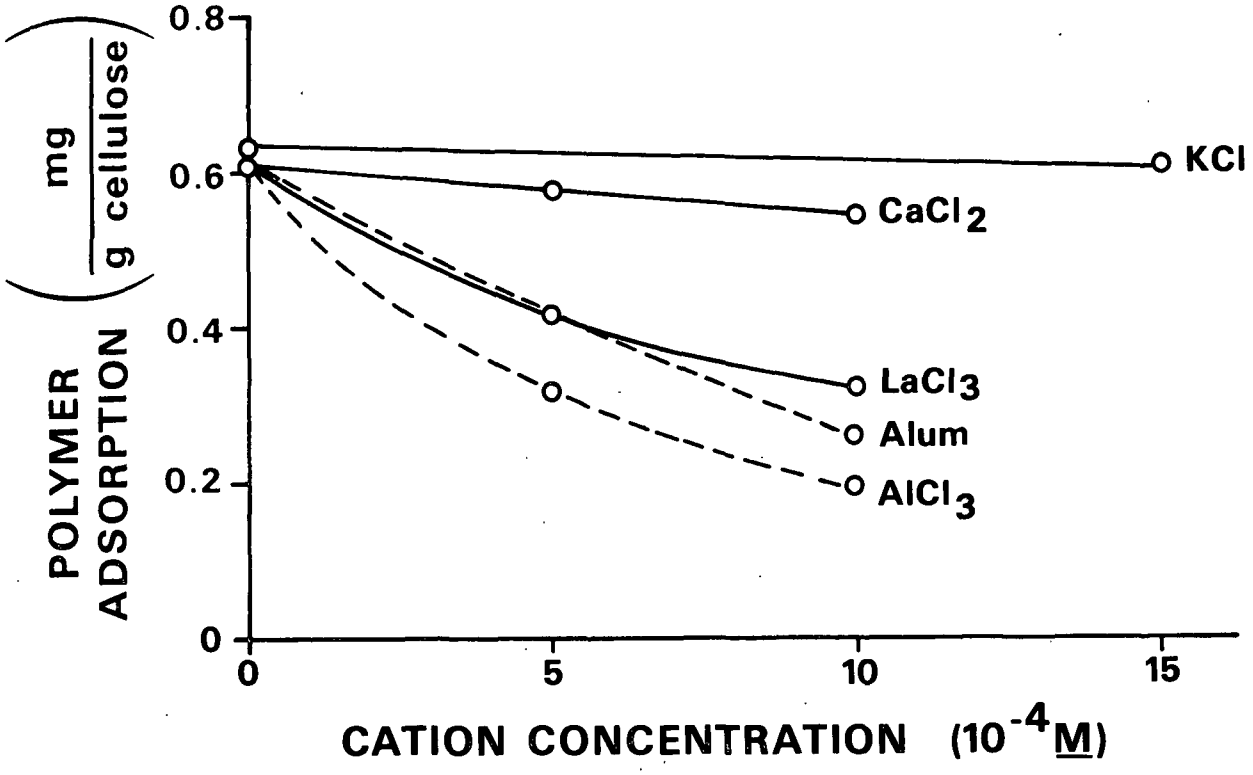

Figure 50. Polymer adsorption as a function of cation concentration and valence (3.0 ppm polymer addition; pH = 4.1; 0.01N KCl background).

The higher valence cations have a larger detrimental effect on polymer adsorption. The effects of lanthanum and aluminum were too large to be explained by the possible effects of the chloride ion (see Fig. 49). Therefore, the effect of cations on polymer adsorption appears to be a function of cation valence and concentration. The effects of aluminum chloride and aluminum sulfate at pH 4.1 closely parallel that of lanthanum chloride. This suggests that the aluminum salts at low pH are detrimental to polymer adsorption due to the trivalent aluminum species. Aluminum chloride, however, has a slightly greater effect than lanthanum chloride. This is possibly due to the smaller ionic radius of the trivalent aluminum ion which increases its charge density and probably its adsorption. On the other hand, aluminum sulfate has a slightly lower effect than aluminum chloride which may be due to the screening of the cationic charge by sulfate ions.

The detrimental effects of aluminum chloride and aluminum sulfate concentration can also be represented in terms of aluminum adsorption. A fairly good correlation exists between the degree of aluminum adsorption and the degree of polymer adsorption (Fig. 51). As aluminum adsorption increases, polymer adsorption decreases.

Aluminum Sulfate Desorption Experiments

Aluminum sulfate desorption experiments were conducted to understand how the polymer adsorbs. Aluminum sulfate was adsorbed for 10 minutes from 5.0 x 10^{-4}M Al solutions at various pH's. Polymer was then adsorbed for 1 minute at 3.0 ppm. After polymer adsorption, the aluminum was desorbed by acidification to pH $\tilde{}$ 3.5. Any polymer which is adsorbed onto the previously adsorbed aluminum should also desorb. However, if the polymer is directly adsorbed onto the cellulose surface, then it should not be desorbed. A cationic surfactant (TDA) was added immediately before acidification to prevent the readsorption of desorbed polymer onto freshly exposed cellulose surface.

The top half of Fig. 52 presents the results of the aluminum sulfate desorption study. The bottom half of Fig. 52 includes a typical aluminum sulfate adsorption curve at 5.0 x 10^{-4}M Al for reference. A curve was also generated with TDA, but without acidification, to determine the effect of TDA on polymer adsorption. The presence of TDA alone, without acidification, produces a typical polymer adsorption curve, thus indicating that TDA has no significant effect on polymer adsorption. The difference between the two curves, with and without acidification, represents the amount of indirectly adsorbed polymer; that is, the amount of polymer which adsorbs onto the previously adsorbed aluminum.

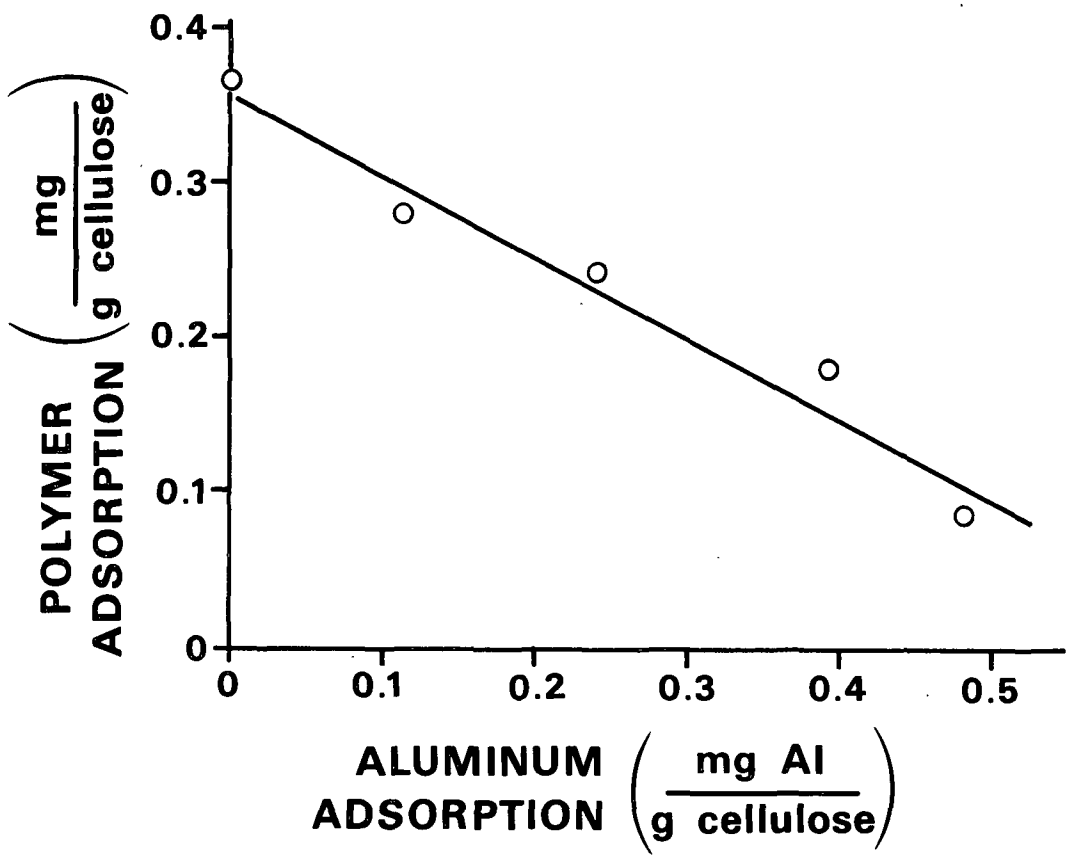

Figure 51. Polymer adsorption as a function of aluminum adsorption at pH 4.1 (1.5 ppm polymer addition).

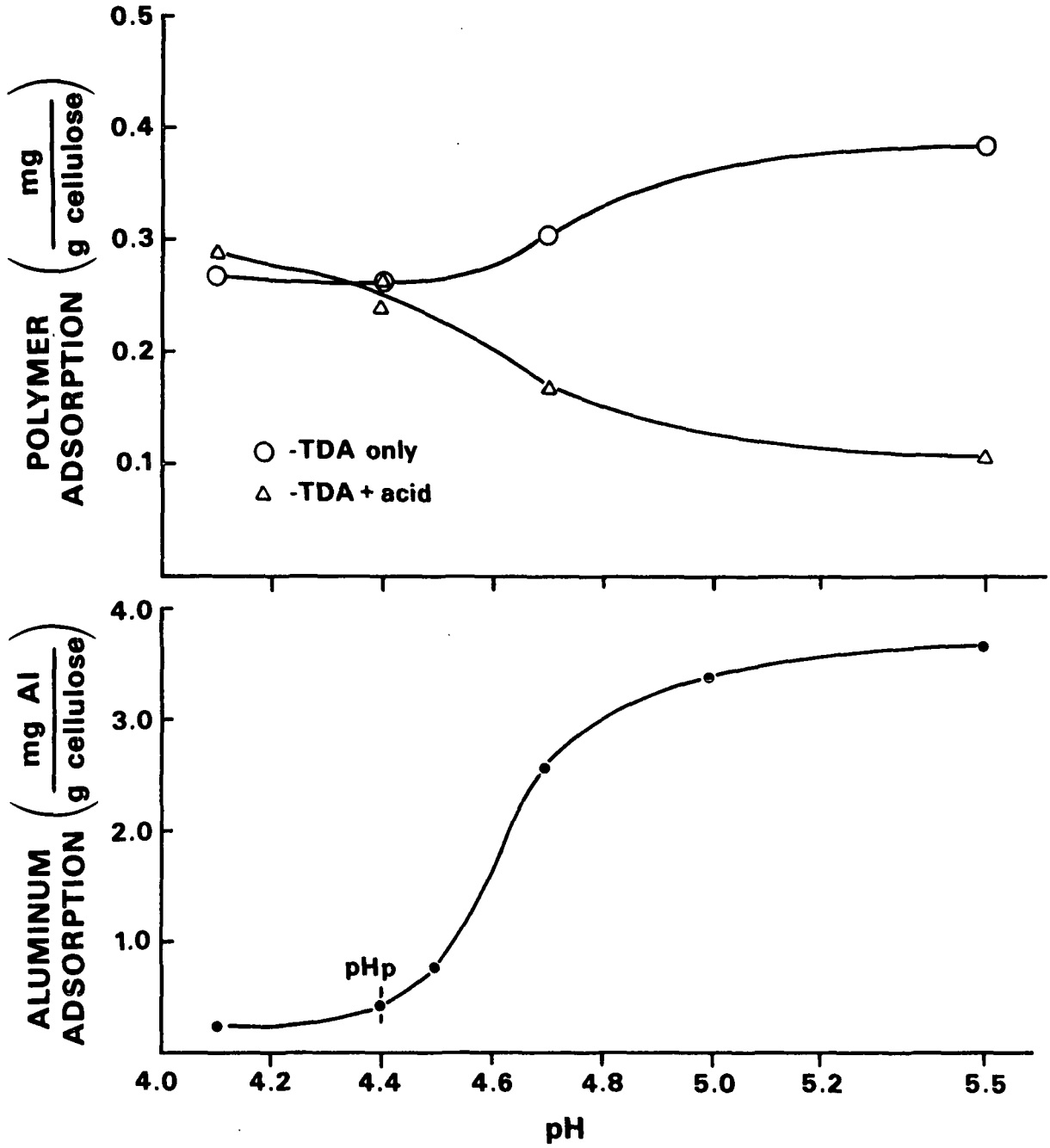

Figure 52. Top: Effect of TDA, acidification and pH on polymer adsorption in the presence of $Al_2(SO_4)_3$ at 1.5 ppm polymer addition and 5.0×10^{-4} M Al (aluminum desorption experiments).
Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (5.0×10^{-4} M Al; no TDA or acid).

The results indicate a large degree of indirectly adsorbed polymer in the aluminum sulfate precipitate region (i.e., above the pHp). However, below the pHp where the soluble aluminum species exist the polymer adsorbs directly onto the cellulose surface. Due to the many similarities in aluminum and polymer adsorption between aluminum chloride and aluminum sulfate below the pHp, the polymer may be presumed to also adsorb directly onto the cellulosic surface below the pHp in the aluminum chloride system.

Effect of Aluminum Addition after Polymer Adsorption

The effect of adding aluminum after 1 minute of polymer adsorption is presented in Table 5. For comparison the polymer adsorption from the normal order of addition (i.e., aluminum first) is also presented. The aluminum concentration was 5.0×10^{-4} M Al, except in the case where polymer is added before aluminum sulfate, in which case it was 10.0×10^{-4} M Al. The polymer concentration was 1.5 ppm for all experiments. Under the normal order of addition the aluminum was first adsorbed for 10 minutes, then the polymer was added and adsorbed for 10 minutes. Under the reverse order of addition the polymer was first adsorbed for 1 minute; then the aluminum was added and adsorbed for 10 minutes. Aluminum adsorption results are not included since no effect was observed.

Table 5. Effect of additive addition order.

		Polymer Adsorption, mg/g cellulose	
	pH	Normal Order	Reverse Order
$AlCl_3$	4.1	0.37	0.38
	5.5	0.05	0.38
$Al_2(SO_4)_3$	5.5	0.43	0.39[a]
No Al	4.1 & 5.5	0.42	

[a] 10.0×10^{-4} M Al.

As seen in the above table, the only significant effect of addition order is with aluminum chloride at pH 5.5. Under the normal order of addition the adsorbed layer of highly cationic aluminum precipitate prevents much polymer from adsorbing. However, if the polymer is added first, the adsorption of the aluminum chloride precipitate has no influence on polymer adsorption, even though the normal level of aluminum adsorption was observed.

Interpretation of the Polymer Adsorption Results

The mechanisms by which aluminum salts influence polymer adsorption function on the surface of the cellulose. If the mechanism had functioned in solution then it could only be due to the screening of charges on the polymer by the aluminum salt anions. However, the anions had, at most, very little effect on polymer adsorption (Fig. 49, p. 100), which could hardly explain the large differences in polymer adsorption after adding the aluminum salts.

Below the pHp - Both Aluminum Salts

Below the pHp, where only soluble aluminum species exist, both aluminum salts reduce the adsorption rate of the cationic polymer. At 15 seconds polymer adsorption time, the polymer adsorption is strongly reduced by aluminum salts. However, after 10 minutes the polymer adsorption is hardly affected by aluminum salts (Fig. 43 and 44, p. 92 and 93). Therefore, aluminum salts below the pHp reduce polymer adsorption by reducing the polymer adsorption rate.

In this pH region, the polymer adsorption rate is dependent upon the adsorption level of the trivalent aluminum species. This is apparent from an experiment comparing the effects of aluminum and lanthanum. In the experiment both aluminum and lanthanum reduced polymer adsorption to a similar extent as their concentrations were raised (Fig. 50, p. 101). Lanthanum, however, does

not hydrolyze below pH 8 and, therefore, exists only in the trivalent form. Since the mechanisms affecting the polymer were determined to occur at the fiber surface, the adsorption of the trivalent lanthanum ion must reduce polymer adsorption. Because the effect of aluminum is very similar to lanthanum, it must also reduce polymer adsorption (i.e., polymer adsorption rate) through the adsorption of a trivalent species. Furthermore, the low dependence of aluminum and polymer adsorption on pH below the pHp suggests that the trivalent aluminum species is preferentially adsorbed up to the pHp.

The predominant adsorption of the trivalent aluminum ion is expected because of its superior charge density and concentration with respect to the other soluble aluminum species (i.e., $AlOH^{2+}$, $AlSO_4^{+}$, $Al_8(OH)_{20}^{4+}$, and possibly a polynuclear aluminum sulfate species). The slightly differing effects of aluminum chloride, aluminum sulfate, and lanthanum chloride on polymer adsorption (Fig. 50, p. 101) may also be explained in terms of charge density and concentration. The trivalent aluminum ion has a smaller ionic radius than lanthanum, hence a greater charge density, and would be expected to adsorb to a slightly greater extent. Therefore, it is not surprising that aluminum chloride has a slightly greater detrimental effect on polymer adsorption. However, aluminum in the presence of the complexing sulfate ion has a slightly lesser effect on polymer adsorption. This may be due to the screening of the cationic charge by sulfate ions.

Polymer, like the soluble aluminum species, adsorbs directly onto the fiber surfaces according to the aluminum desorption results (Fig. 52, p. 104). In the case of aluminum, the small trivalent aluminum ion diffuses very quickly through solution to the fiber surface and rapidly approaches equilibrium during adsorption. At the investigated concentrations ($\leq 10.0 \times 10^{-4}$M) its adsorption

is limited by the equilibrium which is a function of aluminum concentration and the carboxyl content of the pulp. The high molecular weight polymer, however, diffuses through solution much more slowly and its adsorption, therefore, is limited by its adsorption rate. Both aluminum and polymer adsorption raise the fiber charge (Fig. 19 and 25, p. 60 and 72), which reduces the electrostatic attraction between the fiber carboxyl groups and the cationic polymer and thereby decreases the polymer adsorption rate. As a consequence, the relative polymer adsorption (%) is reduced at 15 seconds polymer adsorption time as polymer concentration is increased (Fig. 23, 36, 40-42, p. 69, 84, 88-90). However, the polymer adsorption rate is also a function of unadsorbed polymer. Therefore, the polymer adsorption (weight basis) increases with polymer concentration (Fig. 23, 35, 37-39, p. 69, 83, 85-87), even though the relative polymer adsorption (%) decreases.

Above the pHp - $AlCl_3$

Above the pHp, where the aluminum chloride precipitate exists, polymer adsorption is reduced to an extremely low level (Fig. 32 and 35, p. 79 and 83). The polymer adsorption is doubled when increasing the polymer adsorption time from 15 sec to 10 min (Fig. 43, p. 92), thus indicating that the polymer adsorption is not in equilibrium.

The polymer adsorption above the pHp is also affected by polymer concentration (Fig. 35 and 36, p. 83 and 84). Polymer adsorption increases proportionally with polymer concentration (i.e., constant relative adsorption). This would suggest that the initially adsorbed polymer doesn't significantly alter the fiber surface charge; otherwise it would affect the adsorption efficiency of additional polymer, thus changing the relative adsorption. If the fiber surface charge is not altered, then the surface should continue to adsorb polymer with

time. This further suggests that the polymer adsorption may not be in equilibrium.

The low polymer adsorption level and the independence of fiber surface charge on polymer adsorption can be explained by the adsorption of the strongly cationic aluminum chloride precipitate. According to the interpretation of the aluminum adsorption results, the fiber surface is essentially covered with a layer of highly charged aluminum chloride precipitate. The electrostatic repulsion between the adsorbed precipitate layer and the cationic polyelectrolyte must hinder polymer adsorption. Further support of the hindrance to polymer adsorption comes from another experiment. When polymer is adsorbed before aluminum, aluminum has no detrimental effect on the polymer (Table 5, p. 105). This indicates that the fiber will allow high levels of directly adsorbed polymer in the presence of aluminum chloride if the polymer was not prevented from reaching the surface. But since the polymer adsorption is so low and relatively unaffected by polymer adsorption time when aluminum is adsorbed first, the polymer must be strongly hindered from reaching the fiber surface. The speculated independence of fiber surface charge on polymer adsorption appears reasonable since polymer adsorption should not make the already highly charged adsorbed aluminum layer significantly more repulsive with respect to further polymer adsorption.

Above the pHp - $Al_2(SO_4)_3$

Above the pHp, where the aluminum sulfate precipitate exists, the aluminum has only a small detrimental effect on polymer adsorption (Fig. 33 and 34, p. 81 and 82). This is in sharp contrast with the aluminum chloride precipitate, which strongly reduces polymer adsorption (Fig. 32, p. 79). After 10

minutes of polymer adsorption the aluminum sulfate precipitate has no effect on polymer adsorption (Fig. 44, p. 93), thus indicating that the aluminum precipitate only reduces the polymer adsorption rate. Like the soluble aluminum species the increase in polymer concentration in the presence of the aluminum yields less than a proportional increase in polymer adsorption (i.e., the relative polymer adsorption decreases - Fig. 37-42, p. 85-90). This suggests that the adsorbed polymer increases the fiber charge which affects the further adsorption of polymer.

According to the interpretation of the aluminum adsorption results, the fiber surface is essentially covered with the highly charged aluminum sulfate precipitate. This is further supported by the aluminum sulfate desorption experiments which indicate that most of the polymer adsorbs onto the previously adsorbed aluminum precipitate (Fig. 52, p. 104). Apparently, the layer of adsorbed aluminum precipitate forms a barrier which hinders the direct adsorption of the polymer onto the carboxyl groups. As with the aluminum chloride precipitate, the adsorption of polymer before the aluminum results in no reduction of the adsorbed polymer (Table 5, p. 105).

The adsorption of the polymer onto the previously adsorbed aluminum sulfate precipitate can be explained by (1) the lower charge of the aluminum sulfate precipitate as compared to the aluminum chloride precipitate (Fig. 19 and 20, p. 60 and 61), and (2) the incorporation of negatively charged sulfate ions into the aluminum precipitate. Due to its lower charge (ζ = +11 mV), when compared with the aluminum chloride precipitate (ζ = +24 mV), the aluminum sulfate precipitate must allow more indirect adsorption of the polymer. It may also provide less of a repulsive barrier to direct polymer adsorption. However,

there must be another reason besides a lower cationic charge to explain the increase in polymer adsorption. This is because the soluble aluminum species, which are more detrimental to polymer adsorption, have less of an effect on fiber charge (i.e., ζ = -5 mV). The incorporation of the sulfate ion into the aluminum precipitate suggests a mechanism as proposed by Moore (34). Moore has proposed that the sulfate, which is known to interact with hydroxyaluminum species and even displace hydroxyl groups, can provide sites on the adsorbed aluminum for adsorption of polymer. This is the only mechanism which can explain the high polymer adsorption onto the highly cationic aluminum precipitate.

Near the pHp - $Al_2(SO_4)_3$

The minimum in polymer adsorption near the pHp in the aluminum sulfate system is difficult to interpret, due to the presence of both soluble and precipitated aluminum species. The high charge on the fiber (ζ = +13 mV) indicates that the fiber surface is already essentially covered by aluminum precipitate. However, a significant portion of the aluminum is still in the form of the soluble aluminum species. The adsorbed aluminum precipitate would be expected to reduce the direct adsorption of the polymer, whereas the soluble aluminum species would be expected to screen and adsorb to the negative sites on the fiber (i.e., carboxyl groups and sulfate groups). Possibly as the precipitate reduces the direct adsorption of the polymer, the soluble species reduce the indirect adsorption of the polymer onto the sulfate groups of the precipitate. This conclusion is consistent with the results in the other pH regions.

CONCLUSIONS

ALUMINUM ADSORPTION

In agreement with Arnson's study, the amount of aluminum adsorbed onto a cellulosic fiber was observed to be a function of pH, aluminum concentration, and counterion. The anion from the aluminum salt was found to significantly affect the adsorption of the precipitate species. The divalent sulfate anion, when compared with the chloride anion, was observed to lower the cationic charge on the precipitate-covered fiber and to allow greater adsorption. Unlike the earlier study, aluminum adsorption was found to be a function of aluminum concentration throughout the whole pH and concentration range. In agreement with Arnson's study, a characteristic sharp increase in aluminum adsorption was observed to occur between pH 4-5. However, unlike Arnson's study, the break in aluminum adsorption correlated with the pH at which aluminum starts to precipitate (pHp). The pHp's for aluminum chloride in the presence of fibers were found to be approximately 1.6 pH units lower than the values cited by Hayden and Rubin and the values determined in this study in the absence of fibers. However, the pHp's for aluminum sulfate were in total agreement.

With the understanding of Hayden and Rubin's aluminum distribution curves it was possible to consider the adsorption of aluminum and polymer from aluminum salt solutions in two distinct pH regions. The first region was below the pHp where only soluble aluminum species exist. The second region was above the pHp where the aluminum precipitate was predominant.

Below the pHp, for both aluminum salts, the trivalent aluminum ion was concluded to be the dominant adsorbing species. The preferential adsorption of the trivalent ion was interpreted to be due to its superior charge and

concentration. The adsorption of trivalent aluminum was dependent upon aluminum concentration in the concentration range of 2.5 to 10.0 x 10^{-4}M.

Above the pHp the colloidal aluminum precipitates were the principal aluminum species to adsorb. The composition of the precipitates was found to differ for each of the aluminum salts. With aluminum sulfate at pH 5.5 the precipitate contained approximately 1 mole sulfate per 4.2 moles aluminum. This is in contrast to the precipitate formed in the presence of $AlCl_3$ which cannot contain divalent anions. The precipitate formed in the presence of $Al_2(SO_4)_3$ produced a lower charge on the fibers (ζ = +11 mV) than the aluminum chloride precipitate (ζ = +24 mV). It was suggested that the lower charge from the aluminum sulfate precipitate allowed greater adsorption as compared with the precipitate in the aluminum chloride case. At low aluminum additions (0 to 2.5 x 10^{-4}M) the fiber charge and the adsorption of aluminum precipitate were found to increase rapidly with concentration. In this concentration range an ion exchange mechanism with the carboxyl groups was interpreted to be an important aspect of the adsorption process. At higher concentrations (2.5 to 10.0 x 10^{-4}M) the fiber charge remained constant while the adsorption increased linearly with concentration. In this concentration range it was concluded that the fiber surface was essentially covered by the precipitate and multilayer adsorption occurred.

EFFECT OF ALUMINUM ON POLYMER ADSORPTION

Below the pHp, where the soluble aluminum species exist, both aluminum salts reduced the polymer adsorption. The reduction in polymer adsorption was interpreted to be due to a reduction in adsorption rate. The polymer adsorption (i.e., adsorption rate) was a function of aluminum adsorption, and consequently

aluminum concentration. Polymer adsorption was found to increase with higher polymer concentrations; however, the relative polymer adsorption decreased. Higher polymer concentrations were also observed to have the same effects in the absence of aluminum, thus indicating that it was not due to the influence of aluminum. The detrimental effects of adsorbed aluminum and polymer on the relative polymer adsorption were apparently due to the occupation of the negative adsorption sites (i.e., carboxyl groups) on the fiber and the raising of the fiber charge. The higher fiber charge would reduce the electrostatic attraction between the fiber carboxyl groups and the cationic polymer.

Above the pHp, in the presence of the aluminum chloride precipitate, polymer adsorption was reduced to an extremely low level ($\simeq$ 5%). This would be expected from an unfavorable adsorbing surface, such as the highly charged layer of adsorbed aluminum precipitate. The relative polymer adsorption was found to be unaffected by aluminum and polymer concentration. This was interpreted to be due to the extremely high fiber charge, which is unaffected by further aluminum and polymer adsorption. The relative polymer adsorption was, however, affected by polymer adsorption time, thus indicating that the adsorption was not at equilibrium.

Above the pHp the presence of aluminum sulfate slightly reduced the polymer adsorption. The reduction in polymer adsorption was interpreted to be due to a reduction in adsorption rate. The polymer was found to be adsorbed directly and indirectly onto the fiber surface. Negative sulfate ions were incorporated into the aluminum precipitate. These sulfate ions were interpreted to serve as adsorption sites and improve the adsorption of polymer onto the adsorbed precipitate layer. It was speculated that the lower fiber charge, as compared with aluminum chloride, and the large indirect adsorption of polymer

allowed some of the polymer to eventually become directly adsorbed. However, most of the polymer remained indirectly adsorbed. As with the soluble aluminum species below the pHp, the relative polymer adsorption was observed to decrease with an increase in polymer concentration. This was interpreted to be due to a lower initial fiber charge and higher polymer adsorption, as compared with the aluminum chloride case, which allowed the adsorbed polymer to significantly increase the fiber charge and reduce the relative polymer adsorption.

SUGGESTIONS FOR FUTURE RESEARCH

Electrostatic interactions between the polymer and the fiber surface were interpreted to have a significant effect on the adsorption of the low charge, cationic polyelectrolyte. However, commercial polymers vary greatly in charge characteristics. An investigation of the effect of charge density and charge type would be possible and of great interest. Information gained from such a study would improve the understanding of how polymers interact with aluminum salts during adsorption onto cellulose.

The present study was conducted as one step toward understanding the differing effects of alum on the retention of fine solids in papermaking systems using cationic polyelectrolytes as retention aids. The next step would be to relate polymer adsorption in a system containing aluminum salts to the retention of fine solids. To remain with a well-characterized system, cotton linters fines can first be used as the fine solids. Additional studies can incorporate fillers such as titanium dioxide and filler clay.

Purified cotton linters have served as an excellent model for a cellulose surface similar to that of wood fibers. However, papermaking fibers contain many other substances which may or may not affect the interactions between polymer and aluminum for adsorption. Even though a study involving wood fibers and their impurities may be very complex, the real worth of the present study and the studies suggested above would be the successful application of the results to a commercial papermaking system. Therefore, there is a need to apply the results to more realistic papermaking systems.

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REFERENCES

1. Hayden, P. L.; Rubin, A. J. Systematic investigation of the hydrolysis and precipitation of aluminum (III). In Rubin's Aqueous-Environmental Chemistry of Metals. Ann Arbor, Michigan, Ann Arbor Science, 1974. 317 p.

2. Arnson, T. R.; Stratton, R. A., Tappi 66(12):72-5(1983).

3. Britt, K. W. The fines formation of paper stock. TAPPI CA Report No. 57, Chap. 8 (Sept. 1, 1975).

4. Marton, J., Tappi 57(12):90-3(1974).

5. Arno, J. N.; Frankle, W. E.; Sheriden, J. L., Tappi 57(12):97-100(1974).

6. Frankle, W. E.; Sheriden, J. L., Tappi 59(2):84-8(1976).

7. Moore, E. E., Tappi 58(1):99-101(1975).

8. Pelton, R. H.; Allen, L. H., Colloid and Polymer Sci. 261(6):485-92(1983).

9. Avery, L. P., Tappi 62(2):43-6(1979).

10. Arvela, P.; Swanson, J. W.; Stratton, R. A., Tappi 58(11):86-9(1975).

11. Nicke, R.; Hartmann, H. J., Zellstoff Papier 25(12):360-6(1976). [IPC Translation.]

12. Guender, W.; Auhorn, W., Paper 120 (World Research and Development Issue), 1975:20-35.

13. Arnson, T. R. Characterization of parameters involved in the retention of fines in an unbleached kraft papermaking system. A-291 Special Studies. Appleton, Wisconsin, The Institute of Paper Chemistry, 1976.

14. Arnson, T. R. The adsorption of complex aluminum species by cellulosic fibers from dilute solutions of aluminum chloride and aluminum sulfate. Doctoral Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1980. 143 p.

15. Akit, J. W.; Greenwood, N. N.; Khandelwal, B. L., J. Chem. Soc., Dalton, Trans., 1972:1226-9.

16. Akit, J. W. Nuclear magnetic resonance spectroscopy in liquids containing compounds of aluminum and gallium. In Moody's Annual Reports on NMR Spectroscopy. London, Academic Press, 1972:465-542.

17. Volokhov, Yu. A.; Eremin, N. I.; Mironov, V. E., Issled. Ob. Neorgan. Tekhnolo., 258-61(1972). [IPC Translation T-1833.]

18. Hester, R. E.; Plane, R. A., Inorganic Chem. 3:769-75(1964).

19. Stryker, L. J.; Matijevic, E., J. Phys. Chem. 73(5):1484-7(1969).

20. Ow, S. K. Investigation of the role of sulfate ions in the reaction between tetrahydroabietic acid monolayers and aluminum ions. Doctoral Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1974. 156 p.

21. Kindler, W. A.; Swanson, J. W., J. Poly. Sci. 9, Part A-2, (9):853-65 (1971).

22. Chang, M. Y.; Robertson, A. A., Pulp and Paper Mag. Can. 68(9):T438-44 (1967).

23. Lindquist, G. M. The role of polyelectrolyte charge density and molecular weight on the adsorption and flocculation of colloidal silica with polyethylenimine. Doctoral Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, 1974. 234 p.

24. Eggert, A. R. The role of particle size and molecular weight on the adsorption and flocculation of polystyrene latex with poly(1,2-dimethyl-5-vinylpyridinium bromide). Doctoral Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, 1976. 188 p.

25. Stromberg, R. R. Adsorption of polymers. In Patrick's Treatise on Adhesion and Adhesives. Vol. I, New York, Marcel Dekker, 1967.

26. Fleer, G. J. Polymer adsorption and its effect on colloidal stability. A theoretical and experimental study on the polyvinyl alcohol-silver iodide system. Mededelingen Landbouwhogeschool Wageningen, The Netherlands, 1971: 71-20.

27. Hostetler, R. E.; Swanson, J. W., J. Poly. Sci. 12, Part A-1:29-43(1974).

28. Green, B. W., J. Colloid Interface Sci. 37(1):144-53(1971).

29. Sandell, L. S.; Luner, P., J. Appl. Poly. Sci. 18:2075-83(1974).

30. Klass, C. P.; Sharpe, A. J.; Urick, J. M., TAPPI CA Report No. 57, Chap. 5 Polyelectrolyte Retention Aids, Sept. 1, 1975:55-69.

31. Stratton, R. A., Tappi J. 66(3):141(1983).

32. Strazdins, E., Tappi 57(12):76-80(1974).

33. Kenaga, D. L.; Kindler, W. A.; Meyer, F. J., Tappi 50(7):381-7(1967).

34. Moore, E. E., Tappi 56(3):71-3(1973).

35. MacLaurin, D. J.; Ward, K. IPC Project 1708-A. Literature survey on cotton linters as a papermaking fiber. Appleton, Wisconsin, The Institute of Paper Chemistry, April 13, 1954.

36. Temming, H. Temming linters. Technical information on cotton cellulose. Gluckstadt, Germany, Peter Temming AG., 1966.

37. Luner, P.; Eriksson, E.; Vemuri, K. P.; Leopold, B., Tappi 50(1):37-9 (1967).

38. Luner, P.; Vemuri, K. P.; Leopold, B., Tappi 50(3):117-20(1967).

39. Panshin, A. J.; de Zeeuw, G. Textbook of Wood Technology. New York, McGraw-Hill, 1970. 164 p.

40. Ingmanson, W. L.; Andrews, B. D., Tappi 42(1):29-34(1959).

41. Wilson, K., Svensk Papperstid. 69(10):386-90(1966).

42. Britt, K. W.; Unbehend, J. E., Tappi 57(12):81-4(1974).

43. Arnson, T. R. Unpublished results, 1977.

44. Fritz, J. S.; Schenk, G. H., Jr. Quantitative Analytical Chemistry. 2nd ed. Boston, Allyn and Bacon, 1969. 509 p.

45. Cundall, R. B.; Lawton, J. B.; Murray, D.; Rowlands, D. P., Polymer 20(3): 389-92(1979).

46. Davies, J. V.; Dodgson, K. S.; Moore, J. S.; Phillips, G. O., Biochem. J. 113(3):465-71(1969).

47. Francois, J.; Sarazin, D.; Schwartz, T.; Weill, G., Polymer 20(8):969-75 (1979).

48. Klein, J.; Conrad, K.-D., Makromol. Chem. 181(1):227-40(1980).

49. Arnson, T. R. An investigation of the competition between aluminum salts and a cationic polyelectrolyte for adsorption on cellulose. A-400 Progress Reports II, IV, V, VIII, and X. Appleton, Wisconsin, The Institute of Paper Chemistry, 1977-79.

50. Arnson, T. R. A-400 Progress Reports IV and X. Appleton, Wisconsin, The Institute of Paper Chemistry, 1977-79.

51. Arnson, T. R. A-400 Progress Report X. Appleton, Wisconsin, The Institute of Paper Chemistry, 1979.

52. Kenchington, A. W. Analytical information from titration curves. In Alexander and Block's Analytical Methods of Protein Chemistry. New York, Pergamon Press, 1960. 353 p.

53. Hirch, P., Rec. Trav. Chim. 71:525-44(1952).

54. Fishman, M. J., Atomic Adsorption Newsletter 11(2):46-7(1972).

55. Sikora, M. D. The role of polyelectrolyte charge density in the mechanism of hydrodynamic shear-induced restabilization of a flocculated colloidal dispersion. Doctoral Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1978. 170 p.

56. Gast, J. C., Hercules Incorporated, Wilmington, Delaware, Personal communication, 1983.

57. Brigham, K. M., The Institute of Paper Chemistry, unpublished work, 1983.

58. Ekwall, P.; Bruun, H. H., Tappi 37(7):303(1954).

59. Ninck Blok, C. J. J. The sizing of paper as a colloidal chemical phenomenon. Doctoral Dissertation, The University of Utrecht, The Netherlands, 1952.

60. Dahl, S. The reaction of alum with paper pulps. Nat. Bur. Std. Report 9847, U. S. Dept. Commerce, Nat. Bur. Std., Washington, D.C., May 24, 1968.

61. Dahl, S. The reaction of alum with cation exchange cellulose. Nat. Bur. Std. Report 10,154, U. S. Dept. Commerce, Nat. Bur. Std., Washington, D.C., Jan. 23, 1970.

62. Davison, R. W. Alum and related materials in papermaking. TAPPI CA Report 57, 1975. 71 p.

63. Linke, W. F., Tappi 45(4):326-33(1962).

64. Reynolds, W. F.; Linke, W. F., Tappi 46(7):410-15(1963).

65. Matijevic, E.; Bell, A.; Brace, R.; McFadyen, R., J. Electrochem. 120(7): 893-9(1973).

66. Matijevic, E.; Brace, R., J. Inorg. Nucl. Chem. 35:3691-705(1973).

67. Adamson, A. W. Physical Chemistry of Surfaces. 2nd ed. New York, Interscience Publ., 1967. 747 p.

68. Handbook of Chemistry and Physics, 56th ed., Cleveland, Ohio, CRC Press, Inc., 1975-76.

69. Kalidas, C.; Knoche, W.; Papadopoulos, D., Ber. Bunsenges. Phys. Chem 75: 106-10(1971).

70. Deltek, H.; Stol, R. J.; DeBruyn, P. L., J. Colloid Interface Sci. 64(1): 72-89(1978).

APPENDIX I

POLYMER SYNTHESIS

SYNTHESIS OF CARBON 14 LABELED COPOLYMER OF ACRYLAMIDE AND METHACRYLAMIDOPROPYLTRIMETHYL AMMONIUM CHLORIDE

The reaction scheme of the polymer is shown in Fig. 53. A detailed description of the polymer synthesis is given in the following sections.

POLYMERIZATION

Dimethylaminopropyl methacrylamide (1.88 mL, 14.9 mmoles), acrylamide (13.5 g, 190 mmoles), EDTA (15 mg), and water (125 mL) were placed in a beaker. The pH was then adjusted to 5.0 with 1.2N HCl. This mixture was then placed in a reaction flask and degassed with oxygen-free nitrogen for 20 minutes using the experimental apparatus shown in Fig. 54. The initiator, azo-bis isobutyronitrile (85.0 mg/3.0 mL acetone), was then added to the reaction flask, and the assembly lowered into the hot oil bath at 60°C. The reaction was run 40 hours under nitrogen atmosphere.

After approximately 45 minutes, the solution was too viscous for degassing, and the nitrogen tube was raised to above the surface of the solution. After approximately 2 hours, the solution was too viscous for the magnetic stirrer. After 40 hours, the final solution was a clear gel.

POLYMER RECOVERY - FIRST PRECIPITATION

The polymer was recovered in the following manner: (a) the polymer was put in solution in distilled water (1600 mL) at 0.5% solids, (b) the solution (completely dissolved) was dripped slowly into a nonsolvent of methanol: acetone (1:1, 14 liters), and (c) the higher molecular weight polymer was

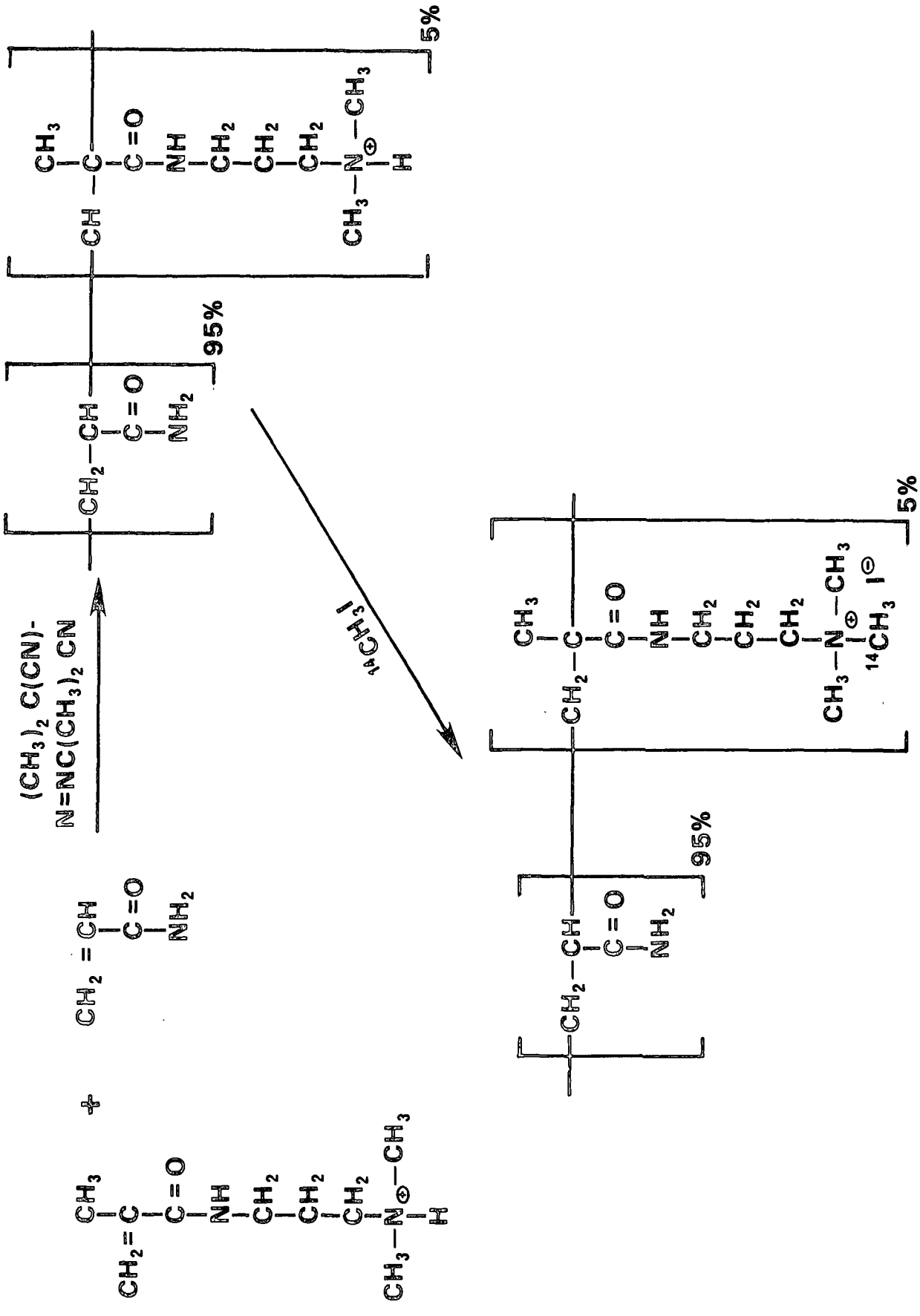

Figure 53. Reaction scheme of polymer synthesis.

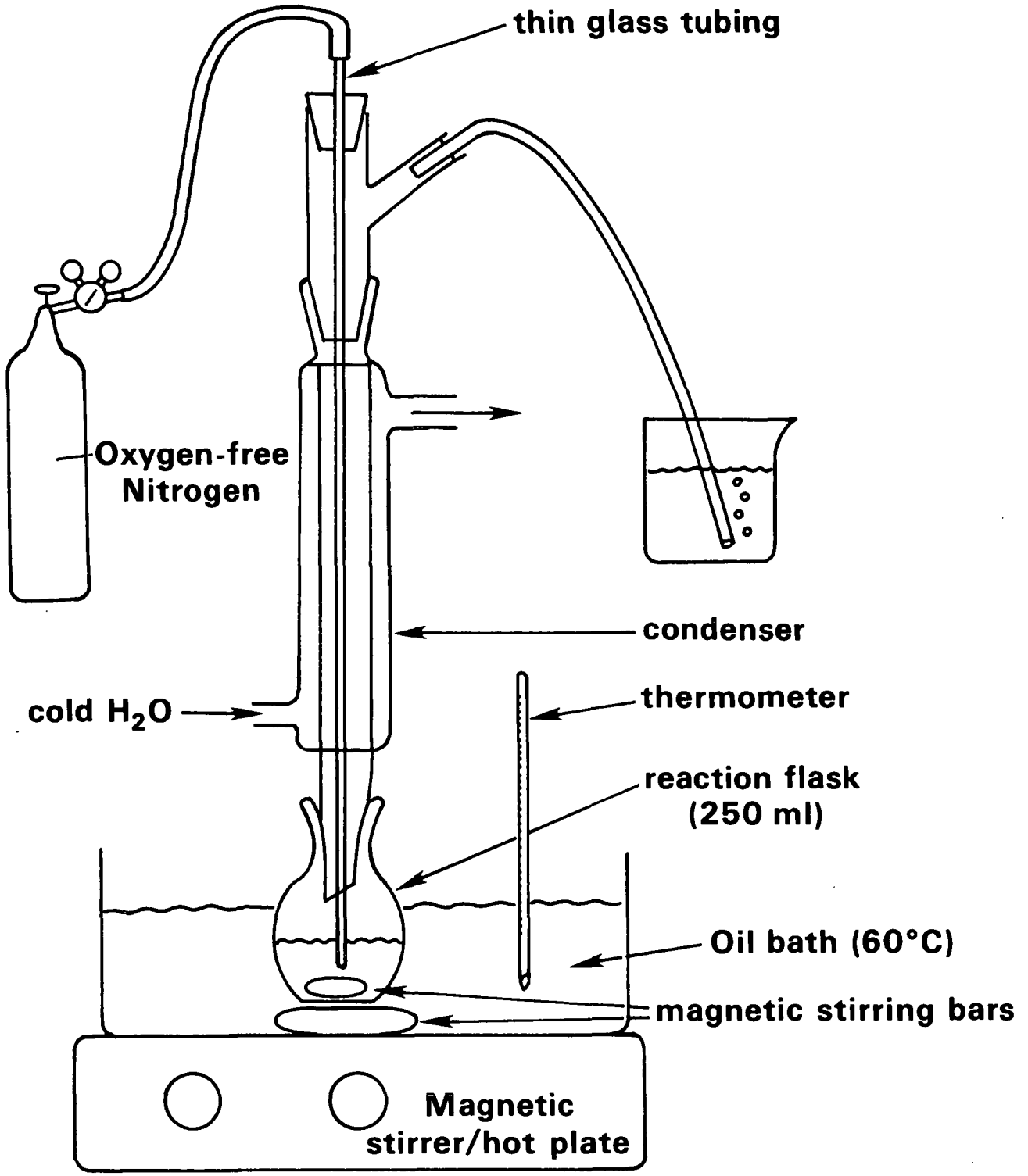

Figure 54. Reaction apparatus for polymerization (schematic).

separated from the soluble low molecular weight polymer with a combination of decantation and filtration operations.

DEPROTONATION

The recovered polymer from the last step was dissolved in 110 mL of distilled water (pH = 5.0). To 1 liter of this solution was added enough 0.1N NaOH to raise the pH to 11.0 (approx. 100 mL 0.1N NaOH). The polymer was deprotonated to increase its reactivity toward methyl iodide in the quaternization reaction. The next two steps (precipitations) were conducted immediately afterward to remove the water and prevent hydrolysis.

PURIFICATION - SECOND PRECIPITATION

The polymer was precipitated in acetone:methanol (1:1, 8 liters) to remove the nucleophilic water and hydroxyl ions. The polymer was then dissolved in 650 mL of freshly purified formamide (nonnucleophilic).

PURIFICATION - THIRD PRECIPITATION

The polymer was again precipitated to remove any residual water and hydroxyl ions. This time chloroform and acetone (1:1, 6 liters) were used to precipitate the polymer. The use of a more nonpolar, nonsolvent mixture was necessary since the formamide accompanying the polymer (as compared with water) will enhance the polarity of the nonsolvent solution.

The polymer was dissolved in 230 mL of freshly purified formamide. Note: After this last precipitation it was important to use freshly purified formamide and to conduct the remaining steps (through the quaternization step) as quickly as possible to minimize the formation of nucleophilic decomposition products in the formamide.

POTENTIOMETRIC TITRATION

A potentiometric titration was conducted on the polymer solution to determine its concentration. The concentration determined the amount of CH_3I needed to quaternize 72% of the tertiary amine groups. Note: Trial quaternizations with $^{12}CH_3I$ indicated approximately 100% reactivity of the $^{12}CH_3I$ up to 72% quaternization. Further additions of $^{12}CH_3I$ had no effect on the quaternization yield. To prevent competition between the $^{12}CH_3I$ and $^{14}CH_3I$ only enough CH_3I was added to quaternize 72% of the tertiary amine groups.

QUATERNIZATION REACTION

100 mL of polymer solution (≈ 3.5 g polymer; 2.3 mmoles cationic groups) was placed in a Teflon container.

1 mL of $^{12}CH_3I$ was diluted with 23.29 mL acetone, then 1 mL of this (0.6608 mmoles $^{12}CH_3I$) was added to 11 mL of purified formamide.

3 mL of acetone was added to an ampoule containing 1 mmole $^{14}CH_3I$. The contents were then added to the 11 mL of formamide (see above). The formamide solution was then added to the polymer solution.

After the addition, the Teflon container was quickly pressurized to 80 psig with N_2 and placed in a 55-60°C mineral oil bath for 3.75 hours.

RECOVERY OF QUATERNIZED POLYMER - FOURTH PRECIPITATION

The polymer solution was precipitated in chloroform:acetone (1:1, 1.75 liters) to remove the formamide. The polymer was then dissolved in 300 mL of distilled water, subjected to a vacuum to remove residual organic nonsolvents, and then freeze dried.

POTENTIOMETRIC ANALYSIS OF THE POLYMER

A potentiometric titration curve of the polymer solution exhibited a large degree of buffering in the lower pH region. The buffering at the lower pH indicated the presence of carboxylic acid groups on the polymer. The degree of buffering corresponded to the presence of approximately 1.0 mole percent carboxylic acid groups. This was undesirable since the polymer was supposed to represent a low charge cationic polymer. Therefore, an esterification procedure using diazomethane was developed. After development, a trial sample of the ^{14}C labeled polymer (0.5 g) was successfully esterified. A potentiometric analysis revealed 100% esterification. A large batch of polymer was then esterified according to this same procedure which is described next.

POLYMER ESTERIFICATION

3.0 g of ^{14}C labeled polymer was dissolved in 150 mL of freshly purified formamide. To this solution was added 10 mL of dry methanol and 2 mL of trimethyl orthoformate. Diazomethane in ether was then added in 15-mL increments to avoid precipitation of the polymer. After each 15-mL addition the solution was subjected to a vacuum using a dry ice-acetone trap to remove the ether. After approximately 50 mL of addition the polymer solution remained yellow, thus indicating an excess of diazomethane. The polymer solution was allowed to sit an hour in the presence of excess diazomethane, and then the solution was subjected to vacuum.

POLYMER RECOVERY

The polymer solution was immediately precipitated in 2 liters of acetone. The polymer precipitate was then removed by filtering. Next, the polymer

was dissolved in 150 mL water while monitoring the pH and neutralizing with 0.1N HCl.

To insure removal of formamide the polymer was again precipitated in 2 liters of acetone. This time the precipitate could not be removed by filtration. Therefore, as much polymer as possible had to be removed by decantation. The recovered polymer was then dissolved in 300 mL of water, along with 0.5 g of ^{14}C polymer from the small batch trial. After freeze drying the yield was 1.65 g.

APPENDIX II

NET CHARGE ANALYSIS OF POLYMER

DESCRIPTION

A brief description of this analysis and the principles involved is given in the experimental section under "Cationic Polyelectrolyte."

REAGENTS

Cationic dye stock solution - approximately 12.4 mg of o-Toluidine Blue per liter of distilled water was prepared in a 1-liter polypropylene volumetric flask. Due to the rapid initial adsorption of dye onto the container walls, the solution was allowed to age at least one week. New solutions were prepared in the same uncleaned flask to prevent the rapid initial adsorption.

Anionic polymer stock solution - Approximately 11 microequivalents polyvinylsulfuric acid potassium salt (PVSK) per liter of distilled water was prepared in a 1-liter glass volumetric flask.

Anionic polymer calibration solution - Two microequivalents PVSK per liter of distilled water were prepared in a 1-liter glass volumetric flask.

Unknown polymer solution - Assuming a 5-mole-percent charged polymer, a solution containing 2 microequivalents of unknown polymer per liter of distilled water was prepared.

INSTRUMENT

A Perkin-Elmer UV-visible range spectrophotometer (Model 320) was used for all measurements.

PROCEDURE

Calibration Curve

The slope of the calibration curve was determined with PVSK. Samples were prepared in 50-mL polypropylene containers. Using appropriate amounts of the PVSK calibration solution, 40-mL samples were prepared ranging from 0 to 2 microequivalents/L. Five milliliters of cationic dye solution and 5 mL of water were then added to each sample. The samples were then measured for absorbance at 625 nm in a 10-cm cell. From the resulting data a figure of absorbance vs. concentration was plotted. The slope was then determined and recorded. The slope only had to be determined once.

Equivalent Determination of the Unknown Sample

Unknown samples were prepared using the PVSK stock solution. First 5 mL of PVSK stock solution was added to each container. Then, using appropriate amounts of the unknown polymer solution (assuming 5 mole percent charge), 40-mL samples were prepared ranging from 0 to 2 microequivalents/L and added to the sample containers. Next, 5 mL of the cationic dye stock solution was added to each sample container. The samples were mixed and then measured for absorbance at 625 nm in a 10-cm cell. A graph of absorbance vs. concentration was plotted. The true charge of the unknown polymer was calculated by the relationship below:

$$\text{Charge density of unknown polymer, (mole \%)} = \left(\frac{-\text{ slope of unknown polymer curve}}{\text{slope of calibration curve}}\right)\left(5 \text{ mole \%}\right)$$

APPENDIX III

HYDROLYSIS OF POLYMER

The potentiometric titration data, pH vs. milliliters of 0.10N NaOH for three polymers in water and for the respective blank are shown in Fig. 55. The titration curve for the ^{14}C labeled polymer is similar to that of a low charge quaternary amine commercial polymer (Q5). The dashed curve represents the original tertiary amine polymer before quaternization to form the ^{14}C labeled polymer. The buffering effect at the higher pH's is caused by tertiary amine groups. The ^{14}C labeled polymer and the commercial polymer both possess some tertiary amine groups.

At low pH's buffering is caused by the presence of carboxylic acid groups. Carboxylic acid groups are formed by hydrolysis. Apparently the ^{14}C labeled polymer possesses a slight degree of hydrolysis. By relating the additional sodium hydroxide uptake ($\simeq$ 0.1 mL) to the weight of the polymer titrated (0.38 g) it is possible to calculate the degree of hydrolysis. The ^{14}C labeled polymer possessed approximately 0.25 mole percent hydrolysis.

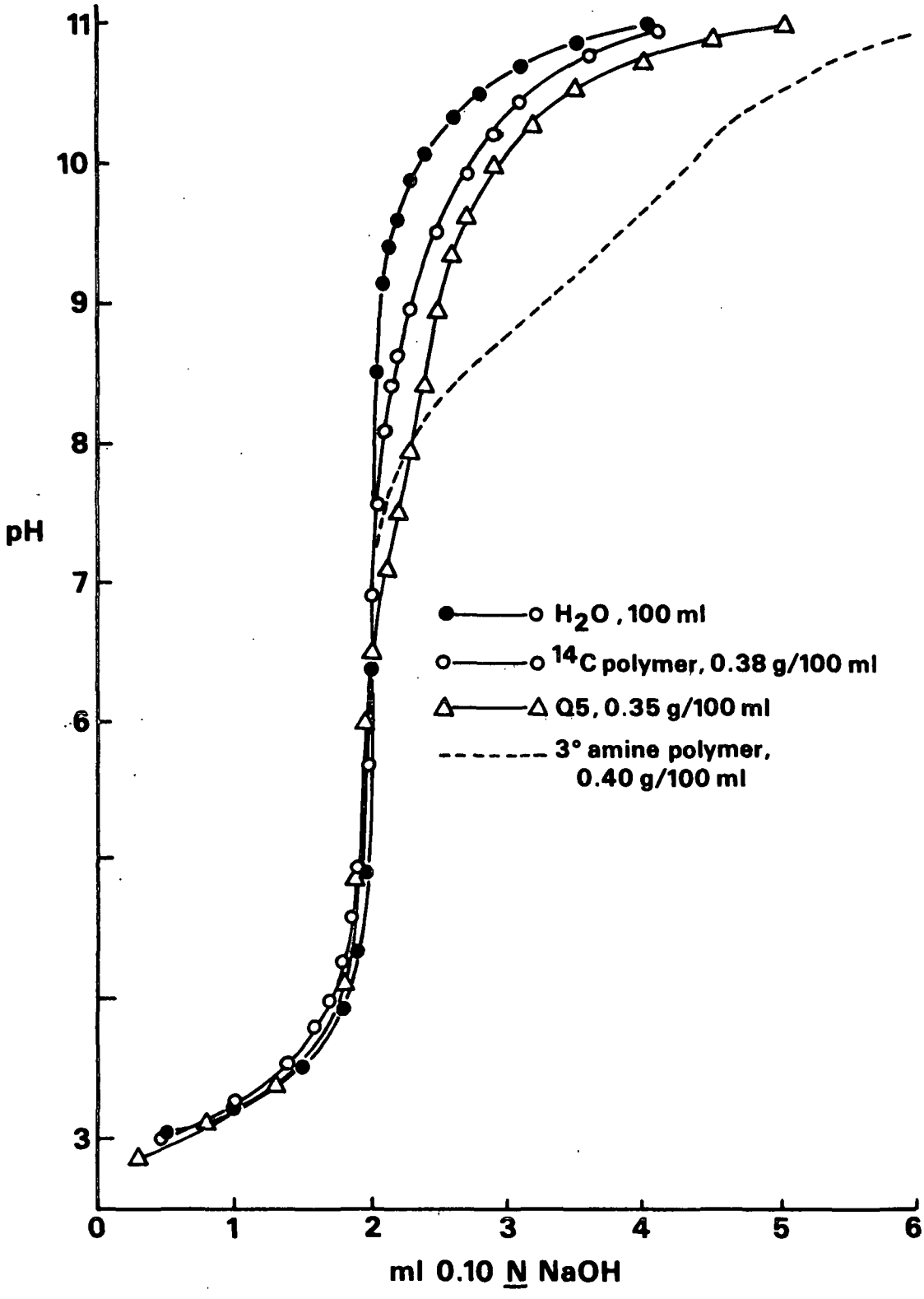

Figure 55. Potentiometric titration curves for water, tagged quaternary amine polymer solution, tertiary amine polymer solution (before quaternization), and a quaternary amine commercial polymer solution (Q5).

APPENDIX IV

MOLECULAR WEIGHT ANALYSIS OF POLYMER

DESCRIPTION

Reduced viscosities were determined using an Ubbelohde viscometer for polymer solutions at 0.01, 0.03, 0.05, and 0.10% solids. Potassium chloride at 0.1N was used to screen the long range effects caused by the charged groups. By extrapolation of the reduced viscosities to zero concentration, the intrinsic viscosity was determined. Using relationships by Francois, et al.[47] and Klein, et al.[48] for polyacrylamide in aqueous NaCl solutions, it was possible to relate the intrinsic viscosity to the molecular weight.

RESULTS

Table 6. Reduced viscosities as a function on concentration.

% Solids	Reduced Viscosities, mL/g
0.01	280
0.03	293
0.05	311
0.10	348

Extrapolation to 0% solids yields $[\eta] = 272$ mL/g. Applying the relationship of Klein, et al.,[48] i.e.,

$$[\eta] = 7.19 \times 10^{-3} \overline{M}_w^{0.77} \ (cm^3/g)$$

yields $\overline{M}_w = 882{,}000$ g/mole. Applying the relationship of Francois, et al.,[47] i.e.,

$$[\eta] = 9.33 \times 10^{-3} \overline{M}_w^{0.75} \ (cm^3/g)$$

yields $\overline{M}_w = 897{,}000$ g/mole.

APPENDIX V

ALUMINUM ANALYSIS

DESCRIPTION

A brief description of this analysis and the principles involved is given in the experimental section under "Aluminum Analysis."

REAGENTS

Buffer solution - 200 g ammonium acetate plus 100 mL concentrated ammonium hydroxide diluted to 1 liter with distilled water.

Chelating solution - 10 g 8-hydroxyquinoline dissolved in 25 mL glacial acetic acid and 25 mL distilled water and then diluted to 1 liter.

PROCEDURE

Aqueous samples containing unadsorbed aluminum were collected from the adsorption runs. When the adsorption runs were conducted at 2.5×10^{-4} M Al or 5.0×10^{-4} M Al, 25-mL samples were used. However, when the adsorption runs were conducted at 10.0×10^{-4} M Al, 10-mL samples were used. The aqueous samples from all runs were collected in 50-mL volumetric flasks. One milliliter of the chelating solution was added to each sample. Then 10 mL of the buffering solution was added to each sample. Immediately after the addition of buffering solution, each sample was shaken, 5-mL volumes of methyl-isobutyl ketone were added to each sample, and then each sample was vigorously shaken for approximately 15 seconds. The aqueous and organic layers were allowed to separate and extra water was added to each sample to bring the ketone layers up into the necks of the flasks. Afterward the samples were allowed to sit for two days to

establish equilibrium. The organic layer of each sample was then pipetted into a 1-cm spectrophotometric cell and measured at 450 nm.

With each set of samples, standard samples were prepared by repeating the adsorption runs without fibers and preparing the samples by the above procedure.

The amount of adsorbed aluminum was calculated from the following relationship and was expressed on a weight/weight basis as mg aluminum per g cellulose

$$\text{Aluminum adsorption} = \left(\frac{A_{std} - A}{M}\right)\left(\frac{C_{std}}{A_{std}}\right)V$$

where A_{std} = absorbance of standard sample

A = absorbance of unknown sample

M = mass of cotton linters pulp, g

C_{std} = concentration of standard sample

V = total volume of solution, L

APPENDIX VI

EXPERIMENTAL DATA: POLYMER ADSORPTION, NO ALUMINUM SALTS

Table 7. Polymer adsorption as a function of addition (No KCl; pH = 5.0; fiber consistency = 0.3%).

Polymer Concentration		Adsorption Time, min	Polymer Adsorption, mg/g cellulose
ppm	mg/g cellulose		
~ 0.3	0.08	10	0.06
	0.09	10	0.06
	0.11	120	0.08
~ 0.9	0.27	10	0.21
	0.29	10	0.24
~ 1.5	0.51	10	0.42
	0.51	10	0.43
~ 2.25	0.75	10	0.62
	0.76	10	0.65
~ 3.0	1.00	10	0.88
	1.01	10	0.86
	1.00	120	0.92
9.0	3.00	10	2.73
~ 18	6.07	10	5.60
60	20.0	90	16.8
120	40.0	90	29.0
300	100.0	90	46.3

Table 8. Polymer adsorption as a function of addition and pH (0.01N KCl; adsorption time = 15 sec).

pH	Polymer Adsorption, mg/g cellulose	
	1.5 ppm Polymer Concentration	3.0 ppm Polymer Concentration
4.1	0.37	0.60
	0.36	0.58
		0.62
4.4	0.38	0.62
		0.60
		0.64
		0.63
4.7	0.39	0.70
	0.40	
5.0	0.39	0.71
		0.70
5.5	0.38	0.70
	0.39	

APPENDIX VII

EXPERIMENTAL DATA: POLYMER AND ALUMINUM CHLORIDE ADSORPTION

Table 9. Adsorption as a function of pH and polymer addition at 2.5 x 10^{-4}M Al (polymer adsorption time = 15 sec).

Adsorption, mg/g cellulose

	Polymer Concentration, ppm		
	0	3.0	
pH	Aluminum Adsorption[a]	Aluminum Adsorption[a]	Polymer Adsorption[a]
4.1	0.15	0.12	0.43
	0.15	0.14	0.45
4.4	0.19	0.23	0.42
	0.23	0.21	0.42
4.5	0.18	0.20	0.39
	0.19	0.23	0.39
4.7	0.43	0.38	0.31
	0.36	0.35	0.31
5.0	1.32	1.28	0.05
	1.26	1.29	0.03
5.5	1.36	1.39	0.06
	1.35	1.28	0.03

[a]Results at each pH obtained on same day with same batch of pulp.

Table 10. Adsorption as a function of pH and polymer addition at 5.0 x 10^{-4}M Al (polymer adsorption time = 15 sec).

Adsorption, mg/g cellulose

	Polymer Concentration, ppm				
	0	1.5		3.0	
pH	Aluminum Adsorption	Aluminum Adsorption	Polymer Adsorption	Aluminum Adsorption	Polymer Adsorption
4.1	0.34	0.23	0.21	0.19	0.32
	0.17			0.27	0.33
4.4	0.48	0.25	0.18	0.50	0.26
	0.20	0.22	0.17	0.29	0.25
4.5	0.50	0.32	0.12	0.55	0.20
	0.22	0.26	0.11	0.37	0.19
4.7	1.48	1.35	0.03	1.24	0.09
	1.42	1.44	0.04	1.32	0.10
5.0	2.07	1.92	0.03	1.80	0.05
	1.88	2.04	0.02	1.71	0.03
5.5	1.96	1.93	0.02	1.85	0.05
	1.83	1.90	0.03	1.84	0.05

Table 11. Adsorption as a function of pH and polymer addition at 10.0×10^{-4} M Al (polymer adsorption time = 15 sec).

Adsorption, mg/g cellulose

	Polymer Concentration, ppm		
	0	3.0	
pH	Aluminum Adsorption[a]	Aluminum Adsorption[a]	Polymer Adsorption[a]
4.1	0.37	0.32	0.19
	0.45	0.44	0.22
4.4	0.54	0.68	0.09
	0.57	0.57	0.08
	0.76	0.60	0.12
4.5	1.45	1.46	0.06
	1.38	1.22	0.08
	1.29	1.23	0.06
4.7	2.24	2.17	0.05
	2.13	2.15	0.06
5.0	2.75	2.56	0.05
	2.57	2.64	0.06
5.5	2.71	2.86	0.05
	2.78	2.79	0.07

[a]Results at each pH obtained on same day with same batch of pulp.

APPENDIX VIII

EXPERIMENTAL DATA: POLYMER AND ALUMINUM SULFATE ADSORPTION

Table 12. Adsorption as a function of pH and polymer addition at 2.5 x 10^{-4}M Al (polymer adsorption time = 15 sec).

Adsorption, mg/g cellulose

	Polymer Concentration, ppm				
	0	1.5		3.0	
pH	Aluminum Adsorption[a]	Aluminum Adsorption	Polymer Adsorption	Aluminum Adsorption[a]	Polymer Adsorption[a]
4.1	0.12	0.12	0.28	0.13	0.51
	0.11	0.12	0.28	0.07	0.54
4.4	0.25	0.25	0.27	0.22	0.49
	0.21	0.22	0.28	0.23	0.46
4.5	0.28	0.23	0.25	0.32	0.44
	0.34	0.30	0.26	0.34	0.50
4.7	0.80	0.68	0.22	0.77	0.39
	0.86	0.58	0.22	0.72	0.38
5.0	1.77	1.58	0.24	1.67	0.45
	1.67	1.70	0.25	1.63	0.45
5.5	1.84	1.78	0.30	1.86	0.61
	1.84	1.65	0.32	1.81	0.60

[a]Results at each pH obtained on same day with same batch of pulp.

Table 13. Adsorption as a function of pH and polymer addition at 5.0×10^{-4} M Al (polymer adsorption time = 15 sec).

Adsorption, mg/g cellulose

	Polymer Concentration, ppm						
	0	0.3		1.5		3.0	
pH	Aluminum Adsorption	Aluminum Adsorption	Polymer Adsorption	Aluminum Adsorption	Polymer Adsorption	Aluminum Adsorption	Polymer Adsorption
4.1	0.26	0.13	0.057	0.20	0.24	0.26	0.42
	0.25	0.17	0.058	0.24	0.24	0.22	0.42
4.4	0.43	0.48	0.050	0.39	0.22	0.49	0.36
	0.43	0.45	0.054	0.45	0.22	0.43	0.37
4.5	0.70	0.88	0.052	0.76	0.21	0.75	0.35
	0.64	0.80	0.053	0.77	0.22	0.70	0.35
4.7	2.50	2.68	0.061	2.54	0.23	2.52	0.38
	2.32	2.55	0.057	2.61	0.23	2.49	0.37
5.0	3.38	3.48	0.072	3.36	0.31	3.36	0.52
	3.34	3.53	0.073	3.38	0.32	3.25	0.52
5.5	3.62	3.80	0.074	3.61	0.34	3.64	0.59
	3.67	3.74	0.078	3.73	0.34	3.65	0.61

Table 14. Adsorption as a function of pH and polymer addition at 10.0 x 10^{-4}M Al (polymer adsorption time = 15 sec).

Adsorption, mg/g cellulose

	Polymer Concentration, ppm				
	0	1.5		3.0	
pH	Aluminum Adsorption[a]	Aluminum Adsorption[a]	Polymer Adsorption[a]	Aluminum Adsorption	Polymer Adsorption
3.9	0.38	--	--	--	--
	0.53	--	--	--	--
4.1	0.49	0.31	0.18	0.32	0.28
	0.42	0.34	0.18	0.43	0.27
4.4	0.75	0.88	0.17	0.60	0.23
	0.81	0.65	0.16	0.74	0.23
	0.94	1.03	0.17		
4.5	2.27	1.94	0.15	2.27	0.27
	2.14	2.26	0.18	2.25	0.27
		1.91	0.17		
4.7	5.11	5.19	0.26	5.36	0.40
	5.10	5.20	0.26	5.13	0.41
	5.20	5.05	0.27		
5.0	6.22	6.06	0.33	6.08	0.55
	6.27	6.29	0.33	6.27	0.53
		6.08	0.31		
5.5	6.37	6.26	0.34	6.16	0.61
	6.52	6.63	0.36	6.34	0.58
	6.55	6.42	0.35		

[a]Results at each pH obtained on same day with same batch of pulp.

Table 15. Adsorption as a function of polymer addition at 20.0 x 10^{4}M Al (polymer adsorption time = 15 sec).

Adsorption, mg/g cellulose

	Polymer Concentration, ppm		
	0	1.5	
pH	Aluminum Adsorption	Aluminum Adsorption	Polymer Adsorption
3.9	0.55	0.68	0.08
	0.41	--	0.08

APPENDIX IX

EXPERIMENTAL DATA: POLYMER AND ALUMINUM ADSORPTION (POLYMER ADSORPTION = 10 MIN)

Table 16. Adsorption as a function of pH and aluminum salt (polymer concentration = 1.5 ppm)

Adsorption, mg/g cellulose

	No Aluminum	$AlCl_3$ (5.0×10^{-4}M Al)		$Al_2(SO_4)_3$ (5.0×10^{-4}M Al)	
pH	Polymer Adsorption	Aluminum Adsorption	Polymer Adsorption	Aluminum Adsorption	Polymer Adsorption
4.1	0.42	0.19	0.38	0.09	0.39
		0.11	0.36		0.38
4.4	0.44	0.31	0.34	--	--
	0.42	0.30	0.35		
4.5	--	--	--	0.53	0.37
				0.74	0.38
4.7	0.42	1.27	0.08	2.83	0.41
		1.32	0.10	2.66	0.39
5.0	0.42	1.91	0.05	3.69	0.43
	0.41	1.90	0.05	3.60	0.41
5.5	0.42	1.85	0.05	3.61	0.43
		1.83	0.05	3.86	0.42

APPENDIX X

EXPERIMENTAL DATA: POLYMER ADSORPTION IN THE PRESENCE OF SIMPLE ANIONS AND CATIONS

Table 17. Effect of anions on polymer adsorption (polymer concentration = 3.0 ppm) (polymer adsorption time = 15 sec).

[KCl], M	Polymer Adsorption, mg/g cellulose	$[K_2SO_4]$, M	Polymer Adsorption, mg/g cellulose
0	0.63	0	0.63
	0.64		0.64
15×10^{-4}	0.61	7.5×10^{-4}	0.62
	0.61		0.61
30×10^{-4}	0.59	15.0×10^{-4}	0.57
	0.57		0.57

Table 18. Effect of cations on polymer adsorption (polymer concentration = 3.0 ppm) (polymer adsorption time = 15 sec).

Cation Concentration, M	Polymer Adsorption (mg/g cellulose) in the presence of: $CaCl_2$	$LaCl_3$	$AlCl_3$	Alum
0	0.62	0.62	0.62	0.62
	0.60	0.60	0.60	0.60
5.0×10^{-4}	0.58	0.42	0.32	0.42
	0.58	0.42	0.33	0.42
10.0×10^{-4}	0.55	0.34	0.19	0.28
		0.32	0.22	0.27

APPENDIX XI

EXPERIMENTAL DATA: EFFECT OF TDA AND ACID ON POLYMER ADSORPTION (ALUMINUM DESORPTION EXPERIMENTS)

Table 19. Effect of aluminum desorption on polymer adsorption (alum at 5.0×10^{-4}M Al) (polymer concentration = 1.5 ppm) (aluminum desorbed by acidification to pH 3.5).

Polymer Adsorption, mg/g cellulose

pH	Polymer Adsorption Time = 1 min	
	TDA + acid	TDA only
4.1	0.29	0.27
4.4	0.27 0.24	0.27
4.7	0.17	0.31
5.5	0.11	0.39

APPENDIX XII

EXPERIMENTAL DATA: EFFECT OF POLYMER AND ALUMINUM ON FIBER CHARGE

Table 20. Zeta potential as a function of polymer addition (0.01N KCl).

Polymer Concentration, ppm	Zeta Potential, mV	
	Average	95% Confidence Interval
0	-12.5	-11.7 to -13.8
1.5	-6.8	-5.75 to -8.3
3.0	0	--
3.9	+2.5	--
7.5	+5.0	+4.45 to +5.6

Table 21. Zeta potential as a function of polymer addition (no KCl).

Polymer Concentration, ppm	Zeta Potential, mV	
	Average	95% Confidence Interval
0	-34	-30 to -36
1.5	-28	-27.5 to -29.5
3.0	-29	-27.5 to -31.0
7.5	-23	-20.7 to -26.0

Table 22. Zeta potential as a function of pH with $AlCl_3$ at 5.0×10^{-4}M Al (0.01N KCl).

pH	Zeta Potential, mV	
	Average	95% Confidence Interval
4.1	-5.8	-4.9 to -7.0
4.5	0	--
4.7	+15.5	+13.5 to +18.0
5.5	+23.0	+21.2 to +25.2

Table 23. Zeta potential as a function of pH with $AlCl_3$ at 10.0×10^{-4}M Al (0.01N KCl).

pH	Zeta Potential, mV	
	Average	95% Confidence Interval
4.05	-5.5	-3.7 to -10.0
4.4	0	--
4.65	+20.0	+19.0 to +21.0
5.5	+23.7	+22.5 to +25.0

Table 24. Zeta potential as a function of pH with $Al_2(SO_4)_3$ at 5.0×10^{-4} M Al (0.01N KCl).

pH	Zeta Potential, mV	
	Average	95% Confidence Interval
4.1	-4.7	-4.2 to -5.5
4.45	0	--
4.6	+13.2	+12.3 to +14.0
5.5	+10.5	+10.0 to +11.0

Table 25. Zeta potential as a function of pH with $Al_2(SO_4)_3$ at 10.0×10^{-4} M Al (0.01N KCl).

pH	Zeta Potential, mV	
	Average	95% Confidence Interval
4.0	-4.8	-3.9 to -6.0
4.25	0	--
4.45	+13.0	+11.7 to +14.5
5.5	+11.0	+10.5 to +11.5

APPENDIX XIII

CORRECTIONS FOR ALUMINUM PRECIPITATE ANALYSIS

After isolating the aluminum sulfate precipitate on cotton linters fibers, the precipitate was desorbed by acidification to pH 3.0. After desorption, the acidified water was drained and analyzed for aluminum and sulfate content. Ion chromatography was used to analyze the sulfate ion content. The concentrations of aluminum and sulfate in the acidified water were:

$$[Al] = 2.42 \times 10^{-4} \underline{M}$$

$$[SO_4^{2-}] = 4.58 \times 10^{-5} \underline{M}$$

Small corrections were then made to account for unmeasured sulfate (HSO_4^- and $AlSO_4^+$) in the ion chromatography analysis and residual filtrate in the fiber pad before acidification.

CORRECTIONS TO ACCOUNT FOR UNMEASURED SULFATE (HSO_4^- AND $AlSO_4^+$)

Only the uncomplexed sulfate (SO_4^{2-}) was measured in the ion chromatography analysis. However, at pH 3.0 sulfate can also exist as HSO_4^- and $AlSO_4^+$ according to the following equilibria:

$$HSO_4^- \underset{}{\overset{K_1}{\rightleftharpoons}} SO_4^{2-} + H^+$$

$$+$$

$$Al^{3+} \underset{K_2}{\rightleftharpoons} AlSO_4^+$$

where $K_1 = 1.20 \times 10^{-2}$[68]

$K_2 = 1550 \pm 400$*

$[H^+] = 10^{-3} \underline{M}$

$[Al] = 2.42 \times 10^{-4} \underline{M}$

$[SO_4^{2-}] = 4.58 \times 10^{-5} \underline{M}$

$$[\text{Total } SO_4] = [SO_4^{2-}] + [HSO_4^-] + [AlSO_4^+]$$

*In dilute solutions 90-99% of the complexed aluminum ($AlSO_4^+$) will exist as an outer-sphere complex.[17,69,70] The equilibrium stability constant for the formation of an outer-sphere complex was found to be 1550 ± 400.[69]

Solving for Total Sulfate

$$[Al^{3+}] + [AlSO_4^+] = 2.42 \times 10^{-4}\underline{M}$$

$$[Al^{3+}] = 2.42 \times 10^{-4} - [AlSO_4^+]$$

$$\frac{[SO_4^{2-}][H^+]}{[HSO_4^-]} = 1.2 \times 10^{-2}$$

$$[HSO_4^-] = \frac{[SO_4^{2-}][H^+]}{1.2 \times 10^{-2}} = \frac{(4.58 \times 10^{-5})(10^{-3})}{(1.2 \times 10^{-2})} = 3.82 \times 10^{-6}\underline{M}$$

$$\frac{[AlSO_4^+]}{[SO_4^{2-}][Al^{3+}]} = 1550 \pm 400$$

$$[AlSO_4^+] = (1550)[SO_4^=][Al^{3+}] = (1550)(4.58 \times 10^{-5})(2.42 \times 10^{-4} - [AlSO_4^+])$$

$$[AlSO_4^+] = 1.604(\pm 0.38) \times 10^{-5}\underline{M}$$

$$[\text{Total } SO_4] = [SO_4^{2-}] + [HSO_4^-] + [AlSO_4^+]$$

$$= (4.58 \times 10^{-5}) + (3.82 \times 10^{-6}) + (1.604 \times 10^{-5})$$

$$= 6.566(\pm 0.38) \times 10^{-5}\underline{M}$$

CORRECTIONS TO ACCOUNT FOR UNADSORBED ADDITIVES PRESENT AS RESIDUAL FILTRATE IN THE FIBER PAD BEFORE ACIDIFICATION

$$[\text{unadsorbed Al}] \quad 4.0 \times 10^{-4}\underline{M} - 2.42 \times 10^{-4}\underline{M} = 1.58 \times 10^{-4}\underline{M}$$

$$[\text{unadsorbed } SO_4] \quad 6.0 \times 10^{-4}\underline{M} - 0.66 \times 10^{-4}\underline{M} = 5.34(\pm 0.04) \times 10^{-4}\underline{M}$$

mL of residual filtrate in fiber pad = 8.7 mL

$$[\text{unadsorbed Al}] \text{ in pad} \quad \frac{1.58 \times 10^{-4} \text{ mole Al}}{1000 \text{ mL}} \times \frac{8.7 \text{ mL}}{0.5 \text{ L}} = 0.03 \times 10^{-4}\underline{M}$$

$$[SO_4] \text{ in pad} \quad \frac{5.34 \times 10^{-4} \text{ mole } SO_4}{1000 \text{ mL}} \times \frac{8.7 \text{ mL}}{0.5 \text{ L}} = 0.93(\pm 0.01) \times 10^{-5}\underline{M}$$

$$[\text{ADSORBED Al}] \quad 2.42 \times 10^{-4}\underline{M} - 0.03 \times 10^{-4}\underline{M} = 2.39 \times 10^{-4}\underline{M}$$

$$[\text{ADSORBED } SO_4] \quad 6.57 \times 10^{-5}\underline{M} - 0.93 \times 10^{-5}\underline{M} = 5.64 \times 10^{-5}\underline{M}$$

PRECIPITATE COMPOSITION

$$\frac{2.39 \times 10^{-4}\underline{M} \text{ Al}}{5.64 \times 10^{-5}\underline{M} \ SO_4} = \boxed{4.24 \text{ moles Al/mole } SO_4}$$